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Ceramic Coatings for High-Temperature Protection of Steel

By William N. Harrison, Dwight G. Moore, and Joseph C. Richmond

A new type of ceramic coating for the protection of low-carbon steel in high-temperature service was developed during the war at the National Bureau of Standards and was used by the Army and Navy on the exhaust systems of certain aircraft and other vehicles. The outstanding features of these coatings are (a) high resistance to chipping under repeated thermal shock, (b) protection of the metal against oxidation during prolonged exposure at temperatures up to about 1,250° F, (c) freedom from the cracking and blistering produced in conventional porcelain enamels under comparable conditions of high temperature and severe thermal gradients, and (d) a mat surface which does not show high lights and, therefore, decreases the visibility.

I. Introduction

Early in the war, crucial shortages of a number of materials essential to its prosecution appeared imminent. The outlook regarding nickel and chromium was particularly dark owing to the greatly increased demand that was anticipated for these metals as constituents of alloys, and also because normal importation of these ores was endangered.

In an effort to alleviate this situation, a project was undertaken at the National Bureau of Standards with a view to the possible replacement of nickel-chromium alloys by ceramic-coated steel in a number of high-temperature applications. The exhaust manifolds of certain automobile engines had for some years been coated with the conventional type of glossy porcelain enamel, and the use of this type of glossy coating was proposed by a number of organizations in the industry. The work at the Bureau included the testing of such coatings submitted by manufacturers, but, in addition, it involved the development of a new type of ceramic coating having properties peculiarly suited to high-temperature use.

When the development work was begun in 1942, it was recognized that there were several properties which were of especial importance in a coating for the intended purpose. These include the following: 1. It should adhere well to the metal; 2. The coating should be thin, both to reduce weight and to minimize the likelihood of cracking and chipping due to accidental mishandling; 3. There should be no "reboil";[1] 4. It should protect the steel against oxidation when used at high temperatures for prolonged periods; 5. It should have high resistance to thermal shock and to temperature gradients.

Such a new type of coating was developed and was described to the armed services in June 1943 in a report also containing comparative data on conventional type porcelain enamel coatings. The present paper comprises most of the information in that initial report, as well as supplementary material on service tests, compositions, and technic of application as used in regular production of exhaust parts for the armed services.

II. Development of High-Temperature Ceramic Coatings

1. Study of Refractory Admixtures

After a consideration of the previously outlined properties that were desirable in a high-temperature protective coating, it was concluded that a coating of greater refractoriness than that of con-

[1] "Reboil" may be defined as the appearance in the coating of gas bubbles usually occurring at or near 1,100° F when porcelain-enameled iron or steel is reheated after the first firing operation.

ventional ground coats would be required. In order to achieve this property, it was believed most promising to add refractory mill additions [2] to the conventional-type enamel ground-coat frit [3] rather than to make the frit itself highly refractory, which would involve its being difficult to handle in the smelting furnace. It was also believed desirable to depart from the conventional glossy enamel finish and to develop a mat surface that, in conformity with military practice, would have low visibility because of its freedom from high lights.

To accomplish these purposes, various refractory materials, singly and in combination, were added as mill additions in varying amounts to conventional ground coat enamel frits. Batch compositions of the two base frits used,[4] together with the computed chemical compositions, are given in table 1. The admixtures that were tried included zirconium oxide, titanium dioxide, ferric oxide, aluminum oxide, chromic oxide, silicon dioxide, silicon carbide, feldspar, mullite, and chrome ore.

TABLE 1.—*Batch weights and computed chemical compositions of ground coat porcelain enamel frits 1 and 11*

BATCH WEIGHTS

Ingredient	Parts by weight	
	Frit 1	Frit 11
Feldspar	31.0	31.0
Flint	11.4	18.0
Borax	37.1	37.1
Soda ash	5.9	5.9
Soda nitre	3.8	3.8
Fluorspar	9.0	3.0
Cobalt oxide	0.5	0.5
Nickel oxide	.4	.6
Manganese oxide	.9	1.1
	100.0	101.0

COMPUTED CHEMICAL COMPOSITION

SiO_2	40.9	49.2
Al_2O_3	7.7	7.7
B_2O_3	17.5	17.4
CaO	8.4	2.9
K_2O	4.5	4.5
Na_2O	15.3	15.2
F_2	3.5	.04
NiO	0.5	.7
CoO	.6	.6
MnO_2	1.2	1.4
	100.1	100.0

[2] A mill addition is any material placed in the ball mill prior to the grinding of the coating for application to the metal.

[3] Frit is a term used in the enamel industry to refer to the material resulting from the quenching and shattering of the molten glass as it is poured into cold water from the smelting furnace.

The coatings, as prepared from the two frits with the various refractory admixtures, were applied to low carbon steel specimens and fired at temperatures up to 1,650° F. They were then examined for surface texture and adherence. The ones showing promise were heated for periods of several hours at a temperature of 1,650° F in order to obtain rapidly an indication of their effectiveness. In these early heating tests, chipping, "burn-off," flow of the coating, and blistering were common defects. Of the various coatings included, those containing alumina showed the best possibilities.

It was noted early in the work that alumina had a very powerful effect in raising the viscosity of the coatings. During firing, the *A–19* coating (table 3) was not "tacky" like an ordinary ground coat, and accidental touching of the coating with firing tools at 1,600° F did not cause sticking. At a temperature of 1,200° F, specimens protected with coatings high in alumina would not adhere to each other, even when placed in intimate contact. To obtain more specific comparisons, frit 11 was dry-ground in a pebble mill to a fineness such that about 1 percent was retained on a No. 200 sieve. At the same time, a number of oxide admixtures were ground to approximately the same fineness.

Mixtures were prepared from the resulting fine powders in the ratio 80 percent by weight of frit to 20 percent of oxide. A solution of gum arabic was added in sufficient quantity to give coherence, after which cylinders 5/8 in. in diameter were dry-pressed at 10,000 lb/in^2. After the cylinders had dried they were reduced to a uniform length of 3/4 in.

Before firing each cylinder it was placed on a small plaque of stainless steel that had been sprinkled with a thin layer of finely divided calcined alumina. The cylinders were then inserted in a vertical position into a furnace at 1,600° F for 10 minutes, after which they were removed and cooled slowly to room temperature.

Figure 1 shows the results of these tests. Frit 11 with no addition fused to a button, whereas the same frit with the 20 percent by weight of *A–1* alumina merely sintered and maintained its

[4] W. N. Harrison, R. E. Stephens, and S. M. Shelton, Consistency of eight types of vitreous enamel frits at and near firing temperatures, J. Research NBS 20, 39 (1938) RP1063.

original sharp edges. The other oxide admixtures were not particularly effective in reducing the high-temperature flow of the frit. The larger size of the chromic oxide and iron oxide buttons in relation to the others is caused by a bubble structure and indicates a gas-forming reaction during the firing operation.

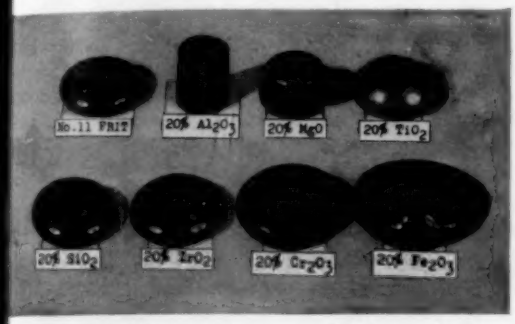

FIGURE 1.—*Effect of 20-percent admixtures of various oxides on the fusion properties of a "hard" porcelain-enamel ground-coat frit when prepared as cylinders 5/8 in. in diameter by 3/4 in. high and fired for 10 minutes at 1,600° F.*

Note sharp edges remaining on specimen containing alumina.

Early in the study of alumina admixtures it was discovered that the type of alumina grain had a controlling influence on the characteristics of the coating. For example, it was found that fused alumina, or alumina calcined at a high temperature, gave dense, glossy coatings when so fired as to give satisfactory adherence. These glossy coatings all showed reboil when heated to appropriate temperatures. Other grades of alumina, calcined at lower temperatures and available commercially at reasonable cost, gave mat coatings that were free of reboil when substituted in the same formula in like amount. *A–1* alumina (table 2) obtained from the Aluminum Ore Co., East St. Louis, Ill., was of this type and was used as the refractory admixtures in the coatings selected.

All the mat coatings prepared with *A–1* alumina were somewhat porous, and it is believed that this porosity is responsible for the absence of reboil blisters when coated specimens are heated through the range 1,050° to 1,150°F. The reboil gases are apparently able to pass through these porous coatings without blistering, whereas the impervious ness of the dense, glossy types is such as to entrap these gases, with the resultant formation of blisters.

TABLE 2.—*Typical chemical and screen analyses of the A–1 calcined alumina used in the preparation of ceramic coatings*

Typical chemical analysis [1]	
	Percent
Al_2O_3	98.89
Na_2O	.55
SiO_2	.03
Fe_2O_3	.03
TiO_2	.004
H_2O (combined)	.50
	100.00
H_2O (free)	1.25

Typical screen analysis [1]	
Retained on No. 100 sieve	1 to 4
Through No. 100 on No. 200 sieve	40 to 55
Through No. 200 on No. 325 sieve	30 to 40
Through No. 325 sieve	10 to 20

[1] Analysis by Aluminum Ore Co., East St. Louis, Ill.:

2. Compositions of Coatings Selected

Three of the coatings prepared with admixtures of *A–1* alumina were found to be outstanding from the standpoint of appearance, ease of application, and adherence to the metal.[5] The mill additions used in preparing these three coatings (*A–19*, *A–20*, and *A–55m*) are given in table 3. A fourth coating, *A–31*, which also was found to possess certain desirable properties, consists of one cover

TABLE 3.—*Mill batches used in the preparation of ceramic coatings A–19, A–20, and A–55m*

Ingredient	Parts by weight		
	A–19	*A–20*	*A–55m*
Frit 1[1]	50.0		
Frit 11	50.0	100.0	100.0
Calcined alumina [2]	25.0	20.0	15.0
Enameler's clay	10.0	6.0	15.0
Black cobalt oxide	[3] 1.00	[3] 0.25	[3] 0.50
Citric acid crystals	0.05	.05	.03
Water	50.0	50.0	50.0

[1] The ratio of frit 1 to frit 11 may be varied in either direction when the resulting slip is better suited to local plant conditions.

[2] Aluminum Ore Co. *A–1* (see table 2).

[3] This amount of cobalt oxide may be reduced or even eliminated without damage to performance characteristics. The nearly black color imparted by the cobalt is conducive to uniformity of appearance.

[5] Because of the unusual properties of the developed coatings, application was made for a Government patent. This application was originally filed under the provisions of Revised Statute 4814, which served to keep the subject matter in a confidential category. At the end of the war, the need for these restrictions no longer existed, and the patent application was released from this status in December 1945.

coat of *A–20* over a ground coat of *A–19*. Coatings of lower alumina content (10 percent and 5 percent) have been prepared and have less tendency to "burn-off" and have greater refractoriness than conventional porcelain enamels, but the coatings thus formed do not have a durability at high temperatures comparable to that of the *A–19*, *A–20*, or *A–55m* compositions.

Details regarding the milling, application and firing of the coatings are given in section IV–3.

3. Expansivity and Softening Temperatures

Thermal-expansion and softening-point data were obtained with the Fizeau-Pulfrich interferometer [6] by the revised procedure of Saunders.[7] The specimens for these tests were prepared in the following steps: 1. Pressing small disks of the partially dried slip; 2. Cutting out small pegs of the proper size and shape from the dried disk; 3. Firing the pegs on a small 18-gage stainless-steel sheet for 5 minutes at 1,600° F. Annealing was done by heating the specimens to 1,300° F and cooling them at a rate of 3° F per minute through the critical-temperature zone.

The following tabulation gives the coefficient of linear expansion per °C of frit 11 and of three coatings over the range 25° to 400° C:

Material	Expansivity	Interferometer softening temperature	
		°C	°F
Frit 11	9.6×10^{-6}	531	988
Coating *A–55m*	9.6	560	1040
Coating *A–19*	10.2	589	1092
Coating *A–20*	10.3	592	1098

Considering expansion coefficients only, these data would indicate that coatings *A–19* and *A–20* could be applied to low carbon steel, which has a coefficient of approximately 13.6×10^{-6} over the same range, with less residual stresses on cooling than would be the case when a conventional ground coat prepared from frit 11 was applied. Experience has shown, however, that these new coatings cannot be applied in as heavy an application as conventional ground-coat enamels because of spontaneous chipping, a defect which ordinarily indicates an excessively high residual stress between the coating and metal base. The temperature at which stresses are first introduced into the coating during cooling of the coated steel, which is related to the interferometer softening temperature, has an important influence on the residual stress. Coatings *A–19* and *A–20* become rigid at temperatures considerably above that for a normal ground coat, and therefore stresses are being introduced over a wider temperature range during cooling. Thus, although coatings *A–19* and *A–20* have higher thermal expansions than many conventional ground-coat enamels, they may, nevertheless, be under greater stress after cooling to room temperature.

III. Laboratory Tests of Coatings

During the same period that the development work was being carried forward on the ceramic coatings, laboratory tests were being devised that would rapidly give an indication of the relative suitability of the various commercial enamels that were being submitted for the protection of low-carbon-steel exhaust systems. The *A–19*, *A–20*, and *A–31* coatings were developed in time to be included in these tests. The *A–55m* coating, however, was a later development.

In two of the laboratory tests (flame impingement and air-blast thermal shock) the specimens coated with the conventional enamels were submitted by the respective manufacturers. For all other tests, the required enameled specimens were prepared and coated at the Bureau, using the ingredients supplied by the manufacturers. The manufacturers also supplied directions for the preparation, application, and firing.

The recommended firing temperatures for the conventional enamels varied from 1,550° to 1,750° F. The NBS coatings applied for the laboratory tests were fired at 1,600° F.

One of the difficulties in devising suitable laboratory tests for the coatings was to provide conditions that would be representative of those under which aircraft exhaust systems operate. Little information as to the operating conditions was available at that time, but they were known to vary widely. For example, it was reliably reported that some short exhaust stacks, especially those that are only slightly curved, never become hot enough to give a red glow in the dark, even when used on powerful engines. The maximum

[6] George E. Merritt, The interference method of measuring thermal expansion, BS J. Research **10,** 59 (1933) RP515.

[7] James B. Saunders, Improved interferometric procedure with application to expansion measurements, J. Research NBS **23,** 179 (1939) RP1227.

temperature reached by such stacks is presumably below 1,000° F. On the other hand, collector rings for turbo-supercharged engines were known to operate in some instances at temperatures sufficient to give a bright-red color at the hottest parts. The maximum temperature in this case was assumed to be well in excess of 1,250° F. The temperatures suggested by the armed services for many of the tests reported herein (1,100° F and 1,200° F) were chosen to represent intermediate conditions such as are encountered by stacks that are sharply curved near the inlets, and collector rings for some of the engines that are not turbo-supercharged.

Some reported measurements of the temperature of exhaust systems by means of thermocouples attached directly to the outer surface of the metal were so low as to be open to question because of the cooling effect of the surrounding atmosphere on the thermocouple hot junction. Errors can be minimized by spot-welding the respective wires of the thermocouples to the test specimen at slightly separated locations. This method was used in the present study to obtain temperatures of specimens not enclosed in a furnace.

It was observed that the shape of the test specimens had a strong effect upon the behavior of the coatings tested. Some of the test specimens were flat plates (4 in. by 6 in.) instead of being tubular, as in exhaust systems. The flat plates lacked the rigidity of tubes, and the specimens were often distorted by stresses resulting from severe thermal gradients. The effects produced must accordingly be considered as exaggerations of those which would occur in tubular specimens.

1. Flame-Impingement Test

The specimens used in this test were 4 in. by 6 in., and the enamel was applied to both sides of the 18-gage low-carbon steel in thicknesses of 0.003 in. to 0.004 in. A laboratory blast burner having an exhaust tube approximately 5/8 in. in diameter and 3 in. in length was modified, as shown in figure 2, by covering the mixing tube with an enameled cylinder 1 in. in diameter and 9 in. in length. This cylinder was adjusted at an angle of approximately 45 degrees to the horizontal plane in which the specimen was supported, the end being approximately 2½ in. from the specimen. A 22-gage platinum-to-platinum–10-

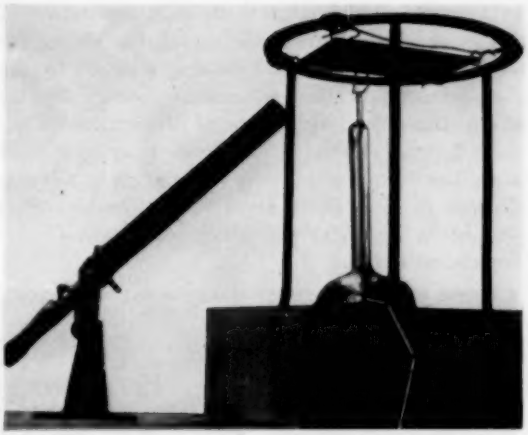

FIGURE 2.—*Equipment used for flame-impingement tests with 4- by 6-in. specimen suspended from tripod.*

The thermocouple beneath the specimen is used to control the flame temperature.

percent rhodium thermocouple was placed at the center of the flame 1/4 in. below the specimen. The air and gas were adjusted so that the thermocouple indicated a temperature of 1,700° ±20° F with a specimen blank in position. When this condition was reached, the blank was removed and the flame was allowed to impinge on a test specimen for 15 minutes, after which the specimen was examined on both sides.

In a trial test the enamel over areas about ⅛ in. in diameter and 1/4 in. apart was ground off the upper surface of the metal base of the specimen, opposite the central point of contact of the flame, and Chromel and Alumel wires were spot-welded at these areas. This thermocouple indicated the temperature of the metal to be 1,040° ±20° F. During the actual tests, however, only the thermocouple shown in figure 2 was used to control the flame temperature.

Among the coatings thus tested, none showed evidence of failure from localized "crawling," in which the enamel separates, leaving streaks of apparently unprotected metal. The failures that did occur from this testing procedure were believed to be accentuated by a flexing, or buckling, of the metal, caused by stresses resulting from large thermal gradients accompanying the localized heating of a small area from the bottom surface. Fine cracks occurred on some specimens of the conventional enamels on the side where the enamel was placed in tension. These cracks

apparently offered a path of least resistance to the gases escaping from the metal, but owing (1) to the constriction of the fissures and (2) to the temperature of the specimens being slightly above the softening points of the enamels, the gases formed elongated blisters or rows of blisters along the lines of rupture of the coating. Varying degrees of this effect from no noticeable effect (condition *A*) to severe effect (condition *D*) are illustrated in figure 3.

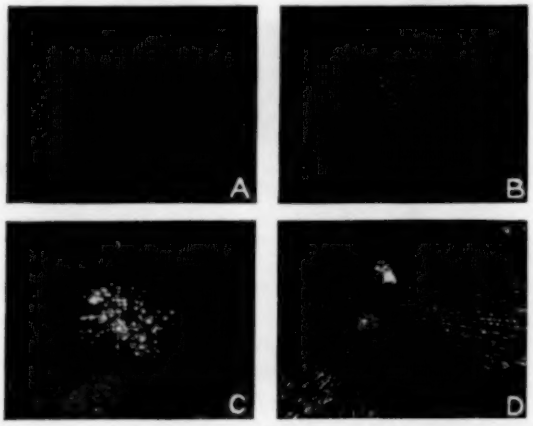

FIGURE 3.—*Tension side of specimens typical of results obtained from both the flame-impingement and the air-blast thermal-shock test, illustrating varying degrees of damage to the coating.*

Condition *A* represents no effect.

The concave (compression) sides of specimens which were distorted by thermal gradients in the flame-impingment test sometimes showed a random distribution of blisters over the test area, illustrated in figure 4 (*II*). On other specimens there was a combination of cracks and blisters shown as condition *III* in the same figure.

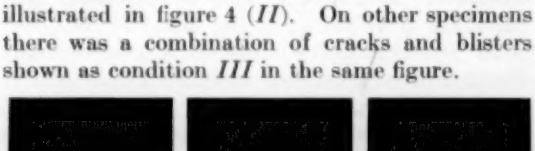

FIGURE 4.—*Compression side of specimens typical of results obtained from both the flame-impingement and from the air-blast thermal-shock test, illustrating different types of damage to the coating.*

Condition *I* represents no effect.

The results of the flame-impingement test are given in table 4. Among the commercial enamels (indicated by *C*, followed by a numeral), *C–9* and *C–5* had the best ratings, both sides of the specimens considered. NBS coatings *A–19* and *A–31* received the maximum rating for both the compression and the tension sides of the specimens.

TABLE 4.—*Results of flame-impingement tests on 4-inch by 6-inch coated specimens made with an indicated flame temperature of 1,700° F and specimen temperature of 1,040° F*

Specimen identification	Average coating thickness		Number of cycles	Condition after treatment	
	Tension side	Compression side		Tension side [1]	Compression side [1]
	Mils	*Mils*			
C–1	4.0	3.8	5	*B*	*II*
C–5	3.3	3.3	5	*B*	*I*
C–6	4.7	4.2	5	*C*	*II*
C–7	2.8	3.0	5	*C*	*II*
C–8	4.2	3.3	5	*B*	*II*
C–9	4.8	4.4	5	*B*	*I*
A–19	2.2	2.1	5	*A*	*I*
A–31	4.1	3.8	5	*A*	*I*

[1] Letter designations refer to condition of test area on tension side of the specimen after treatment, as illustrated in figure 3.

[2] Numerals refer to condition of area on compression side of specimen after treatment, as illustrated in figure 4.

2. Thermal-Shock Test by Air Blast

The specimens for this test were the same as those used for the flame-impingement test (4-in. by 6-in. plates).

Temperature measurements were made by means of Chromel and Alumel wires, separately spot-welded to each specimen after grinding off small areas of enamel at the middle of the test area. A Fisher burner, 1 1/8 in. outside diameter at the top, was placed approximately 1/2 in. below the specimen, which was supported as shown in figure 2, with the thermocouple on the upper side. The temperature of the specimen was allowed to increase rapidly until it reached 1,200° F, at which time a blast of air at room temperature was released on the under side of the specimen. This blast immediately blew out the flame and reduced the temperature of the test area to 400° F within a period of 12 to 15 seconds. After five cycles of this treatment, the specimens were inspected and graded.

The results of the air-blast thermal-shock test are given in table 5. Among the commercial enamels, *C–9* had the highest rating for this test. Experimental enamels *A–19* and *A–31* received the maximum rating for both the tension and the compression sides of the specimens, their condition

after test being shown by *A* in figure 3 and *I* in figure 4.

TABLE 5.—*Results of air-blast thermal-shock test (1,200° to 400° F in 12 to 15 seconds) on 4-inch by 6-inch coated specimens*

Specimen identification	Average coating thickness		Number of cycles	Condition after treatment	
	Tension side	Compression side		Tension side [1]	Compression side [2]
	Mils	*Mils*			
[illegible]4-1	4.8	4.0	5	*C*	*II*
[illegible]4-5	3.4	3.5	5	*C*	*III*
[illegible]4-6	4.6	3.8	5	*B*	*III*
[illegible]4-7	2.8	3.0	5	*C*	*III*
[illegible]4-8	4.3	3.6	5	*D*	*II*
[illegible]4-9	5.6	4.9	5	*B*	[3] *III*
[illegible]4-10	2.0	2.2	5	*A*	*I*
[illegible]4-31	4.2	3.7	5	*A*	*I*

[1] Letter designations refer to condition of test area on tension side of specimen, as indicated in figure 3.

[2] Numerals refer to condition of test area on compression side of specimen, as indicated in figure 4.

[3] Very slight.

3. Thermal-Shock Test by Water Spray

Tubular specimens 1 in. in diameter and 9 in. long, coated inside and out, were mounted as shown in figure 5. The specimens fit snugly into the top of the Fisher blast burner, with little or no leakage at this junction. A refractory tube, approximately 9 in. long, was placed at the top end of the specimen, a close fit being obtained also at this location. By adjusting the air and gas supplies, the flame could be regulated to burn within the enameled metal cylinder for a distance of several inches above the burner. For temperature measurement, Chromel and Alumel wires were spot-welded to the specimen after grinding off small areas of enamel approximately ⅝ in. apart, at a level about 1½ in. above the top of the burner.

At the beginning of the test, the air and gas pressures were so adjusted as to cause the flame to burn within the tubular specimen, the hottest area being at the level of the thermocouple. When the thermocouple indicated 1,200° F, a controlled spray of water was directed at the specimen while the flame still burned inside the tube. The water spray was continued until the specimen was cool enough on the outside for the water to form a film over the area between the points of attachment of the thermocouple wires. This operation required from 12 to 15 seconds for different specimens. Each specimen was given five cycles of this treatment.

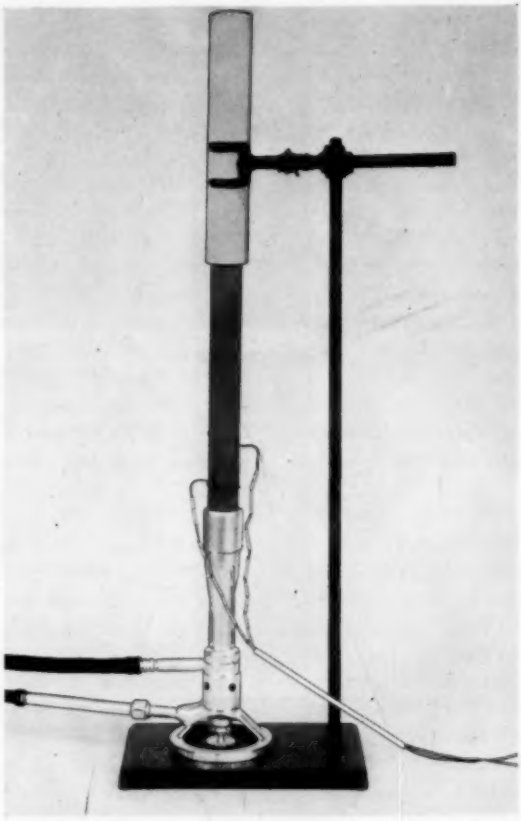

FIGURE 5.—*Equipment for determining resistance of coatings to thermal shock by water spray.*

Specimen is dark tube at center of assembly. Thermocouple wires are separately welded to specimen.

Other tests were made in which the specimens were first quenched from 1,000° F for five cycles and then heated to 1,100° F and allowed to cool without quenching. Still other tests were made in which the specimens were given five quenches from 900° F, after which they were heated to 1,100° F and allowed to cool without quenching.

The results of these tests are given in table 6, in which the specimens are graded by letters. *A* indicates no noticeable effect, as illustrated in figure 6, A; *B* indicates the development of a pebbly surface resulting from blisters, as illustrated in figure 6, B; and *C* indicates chipping of the enamel, as illustrated in figure 6, *C*. This chipping occurred in spots that had first blistered.

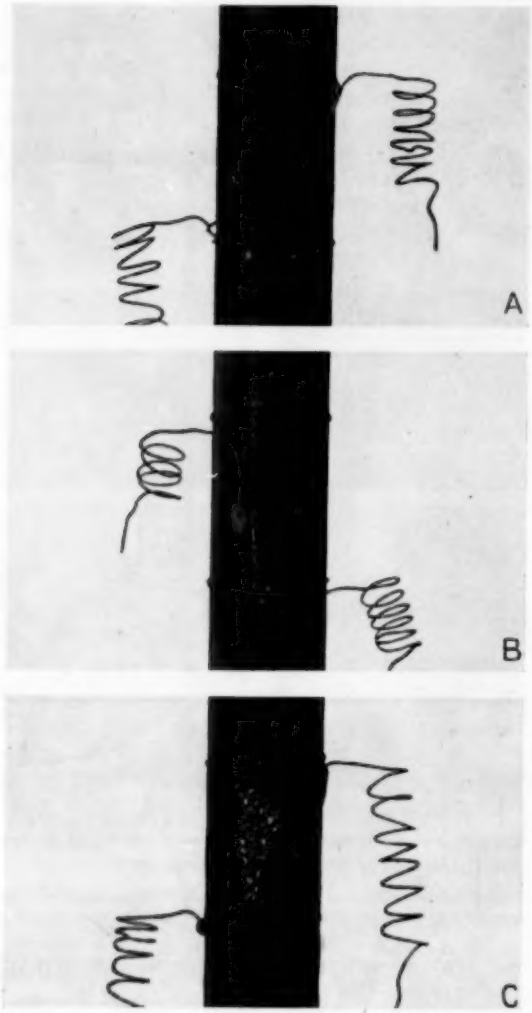

FIGURE 6.—*Three degrees of damage resulting from the thermal-shock test by water spray.*

Condition *A* represents no noticeable effect; condition *B*, a pebbly surface resulting from blisters; and condition *C*, a chipping of the enamel in spots that had first blistered.

As shown in table 6, none of the enamels was affected by five cycles of the water-spray quench from 900° F or 1,000° F. On subsequent heating to 1,100° F, however, damage occurred on all the conventional enamels. Quenching from 1,200° F also damaged all the commercial enamels. Enamel *C–9* was outstanding among the conventional enamels in resisting the more severe temperature conditions. Coatings *A–19* and *A–31* rated grade *A* throughout the water-spray quenching tests.

TABLE 6.—*Results of thermal-shock tests with water spray on 1-inch-diameter coated tubes*

Specimen identification	Average coating thickness	Condition of test area after five quenches from [1]—		
		900° F	1,000° F	1,200° F
	Mils			
C–1	4.0	[2]*A* to *B*	[2]*A* to *B*	*C*
C–5	3.0	*A* to *B*	*A* to *C*	*C*
C–6	3.5	*A* to *B*	*A* to *C*	*C*
C–7	3.5	*A* to *B*	*A* to *C*	*C*
C–8	3.6	*A* to *B*	*A* to *B*	*C*
C–9	3.4	*A* to *B*	*A* to *B*	*B*
A–19	2.3	*A*, *A*	*A*, *A*	*A*
A–31	4.2	*A*, *A*	*A*, *A*	*A*

[1] Letter designations refer to the relative severity of effects, as illustrated in figure 6. *A* indicates no noticeable effect; *B*, blistering; and *C*, blistering followed by chipping.

[2] The first letter in all cases indicates the condition of the test area after five quenches from the indicated temperature. The second letter gives the condition of this same area after subsequent heating to 1,100° F without further quenching.

4. Thermal-Shock Test by Immersion in Water

Flat 18-gage low-carbon-steel specimens 4 in. by 6 in. were used for this test. They were initially heated in an oven, the temperature of which was held slightly above 600° F. A thermocouple was kept in contact with the upper surface of the specimen, and when it indicated that the specimen had reached 600° F, the specimen was removed rapidly from the oven and immediately immersed to a depth of 3 in. (one half submerged) in water at 75°±5° F. The specimen was then examined for damage and, if none had occurred, it was given a second cycle of treatment at an oven temperature of 700° F. In each succeeding cycle the temperature was raised 100° F, and these treatments were continued until failure occurred or until the specimen was quenched from 1,600° F. The temperatures at which failure occurred, as indicated by spalling off of the coating, are given in table 7.

This quenching treatment with the 4 in. by 6 in. plates is probably much more severe than any encountered in service, but the data in table 7 serve to emphasize certain differences among the respective coatings. The "bead" referred to in the third column of table 7 is a very narrow strip of enamel at the extreme edge of a specimen and thicker than over the principal area. With care, beads can be minimized, but they are difficult to eliminate. The powerful effect of thickness upon thermal-shock resistance is evident from the differ-

TABLE 7.—*Thermal-shock tests by immersion in water*

Specimen identification	Average coating thickness	Temperature for failure [1]		
		Chip in bead [2]	Crazing	Failure
	Mils	° *F*	° *F*	° *F*
C-1	3.8	750	----------	1,000
C-5	3.4	700	1,000	1,100
C-7	3.0	750	1,000	1,100
C-8	4.5	750	----------	1,000
C-9	4.2	700	1,000	1,100
A-19	2.0	1,000	----------	1,600+
A-31	4.2	----------	----------	1,200

[1] Temperature from which specimen was quenched to produce failure. A plus value indicates that no failure occurred when quenched from the temperature indicated.

[2] The "bead" is a very narrow strip of coating at extreme edge of specimen, thicker than elsewhere.

ences in the temperatures at which chipping occurred in the beads and those at which failure of the specimens as a whole occurred. It is also notable that coating *A–19*, which did not fail (except at the bead) even when quenched from 1,600° F, had the thinnest coating of all the specimens tested—thinner than a coating of glossy porcelain enamel can be successfully applied in production.

5. Test for Protection of Metal Against Oxidation

As a measure of the degree of protection against oxidation of the metal provided by the various coatings, specimens were heated for prolonged periods at constant temperatures. In these tests it was assumed that there was no appreciable volatilization of the coating ingredients throughout the heating and that the gain in weight that occurred was due to oxidation of the metal. The oxide was in most cases absorbed in the coating as it formed until a saturation level was reached, at which stage the adherence usually deteriorated and the coating flaked off the specimen.

The specimens for the gain-in-weight tests were flat, 18-gage, enameling-iron plates, 1½ in. by 2½ in., having a small hole near one edge, and from which they were suspended during the test. The coated specimens were heated in air in a furnace in which the temperature could be controlled to within ±15 deg. F. The tests were made at 1,400° F for 32 hr, 1,200° F for 77 hr, and 1,000° F for 252 hr.

Specimens were removed for inspection at frequent intervals, and weighings to the nearest milligram were made in order to follow the gain in weight.

A summary of the results of these tests is given in table 8. From these data it is apparent that the rate of oxidation of the coated metal decreases greatly with a decrease in the temperature of test. Both the total amount of weight gain for the entire test period and the rate of gain during the final interval decreased for each coating as the temperature of test was decreased from 1,400° to 1,200° to 1,000° F, even though the length of the test period was increased. Data on experimental coating *A–20* were included in table 8 because tests on coating *A–31* had not been completed at 1,200° and 1,000° F, and it is believed that because of similarity of composition and the relative results obtained at 1,400° F, *A–31* should perform at least as well as *A–20* at the lower temperatures.

TABLE 8.—*Protection provided by different coatings against oxidation of enameling iron at high temperatures as indicated by gain in weight of 1½-inch by 2½-inch specimens*

Specimen identification	Test at 1,400° F				Test at 1,200° F				Test at 1,000° F				
	Coating thickness	Gain in weight			Coating thickness	Gain in weight			Coating thickness	Gain in weight—			
		At 15½ hr	At 32 hr	Rate 15½ to 32 hr		At 15½ hr [1]	At 77 hr	Rate 50 to 77 hr		At 15½ hr	At 78 hr	At 252 hr	Rate 78 to 252 hr
	Mils	*mg*	*mg*	*mg/hr*	*Mils*	*mg*	*mg*	*mg/hr*	*Mils*	*mg*	*mg*	*mg*	*mg/hr*
C-1	3.4	120	156	2.18	3.0	22	41	0.33	3.5	3	8	17	0.052
C-5	3.6	129	[2]	[2]	3.8	15	69	.81	3.4	1	2	5	.017
C-6	3.9	146	223	4.67	3.9	22	99	1.22	4.4	3	7	14	.040
C-7	3.1	100	146	2.79	2.9	16	73	.96	3.6	0	1	2	.006
C-8	3.3	147	212	3.94	3.5	11	69	.85	3.3	1	4	9	.026
C-9	3.6	75	112	2.24	2.8	9	19	.15	3.9	0	0	1	.006
A-19	3.1	25	55	1.82	3.6	12	27	.22	2.4	1	3	6	.017
A-20	2.4	42	69	1.64	2.9	9	21	.19	2.8	1	2	3	.006
A-31	3.3	22	43	1.27	----------	----------	----------	----------	----------	----------	----------	----------	----------

[1] Interpolated.

[2] Specimen chipped before 32 hr.

At 1,400° F, the newly developed coatings *A–19*, *A–20*, and *A–31* gave lower gains in weight than any of the conventional enamels. Enamel *C–9* was outstanding in its low gain in weight among the commercial group.

At 1,200° F, coating *C–9* gave the best results of all the coatings and *A–20* was next. Both of the NBS coatings that were included (*A–19* and *A–20*) permitted less total gain in weight and a lower rate of gain than any of the conventional coatings except *C–9*.

At 1,000° F, the weight gain was low in all cases, but the relative position of coating *C–1* changed, and in this test it had the largest weight gain, whereas *C–9* had the least.

Coated specimens of both enameling iron and SAE 1020 steel were heated for various periods at 1,400° F. Although these comparative data are not shown in table 8, all coatings showed a tendency to chip off the 1020 steel spontaneously after prolonged treatment at 1,400° F, whereas the same coatings on enameling iron, after comparable treatment, still showed fairly good adherence.

6. Tests for Protection of Metal When Heated

When studying adherence of coatings after the oxidation tests, it was noted that some specimens became brittle after prolonged periods of heating at temperatures above a red heat. It was noted also that the time of heating required to produce embrittlement as measured by a standardized impact depended on (a) the temperature, (b) the duration of treatment, (c) the type and amount of alloying, and (d) the protection against oxidation offered by the coating.

The embrittlement test as used in this work consisted in subjecting the specimen to impact at room temperature after various heating periods by allowing a 10-lb weight to fall from a height of 18 in. onto a 1-in.-diameter steel ball centered on the specimen so as to be directly over a 1⅛-in.-diameter by ⅛-in.-deep steel receptacle. Thus, the force of impact depressed the metal sheet over an area represented by the 1⅛-in. diameter of the receptacle and to a depth of ⅛ in. at the center. Failure was indicated by any visible cracking of the metal in this test area.

Table 9 shows the difference in the time at elevated temperatures required to develop embrittlement of the various metals studied. In all cases where comparisons were possible, the application of the *A–31* coating materially increased the time at 1,400° F required for embrittlement failure. Other coatings acted similarly, their effectiveness being closely related to the degree of protection against oxidation. This observation suggests that the cause for the metal becoming brittle is closely associated with intergranular oxidation.

TABLE 9.—*Results of the embrittlement tests*[1] *at room temperature for six metals, both uncoated and coated with A–31, after heating in air at the temperature indicated*

Metal	Time for embrittlement at—		
	1,200° F, uncoated	1,400° F, uncoated[2]	1,400° F, *A–31* coated
	hr	*hr*	*hr*
Ingot iron[3]	>64 but <112	>5 but <11	>200
SAE 1010	>245	>47	>200
SAE 1020	>245	>31 but <47	>200
NAX 9112	>245	>31 but <47	>200
SAE 4130	>245	>47	>200
NE 8630	>245	>31 but <47	>200

[1] Cracking of metal in a standardized impact test, as outlined in text, was taken as embrittlement failure.

[2] Longer heating times than 47 hr not feasible because of oxidation of the metal.

[3] Enameling iron.

TABLE 10.—*Results of tensile-strength tests at room temperature for six steels*

Steel	Tensile strength at room temperature of 18-gage tensile specimens heated—					
	0 hours at 1,200° F.		250 hours at 1,200° F		500 hours at 1,200° F	
	A–31 coated	Bare	*A–31* coated	Bare[1]	*A–31* coated	Bare[1]
	Kips/in.[2]	*Kips/in.*[2]	*Kips/in.*[2]	*Kips/in.*[2]	*Kips/in.*[2]	*Kips/in.*[2]
Ingot iron	46.9	47.3	44.7	19.1	42.8	13.1
SAE 1010	49.2	48.3	45.8	37.0	47.5	30.7
SAE 1020[3]	70.8	71.4	54.3	48.8	50.4	46.6
NAX 9112	83.1	83.1	72.2	63.7	62.9	60.8
SAE 4130[3]	136.8	117.6	75.5	70.0	73.0	63.2
NE 8630[3]	123.2	101.0	78.4	75.6	72.4	52.8

[1] Values in these columns are tensile strengths based on dimensions of the specimens after removal of scale.

[2] *A–31* coating was slightly blistered on these metals, and the resulting punctures in the coating reduced its effectiveness.

None of the data listed in table 9 is strictly quantitative. To overcome this objection, the American Society for Testing Materials tensile

est, E8–42, was used in the hope of obtaining data that would be of value in determining more precisely the effect of the coatings. These data, which are given in table 10, show that in all cases the specimens coated with *A–31* retained more strength than uncoated specimens after having been heated for 250 hr and 500 hr at 1,200° F.

V. Directions for Commercial Application of Coatings

1. Suitable Types of Steels

As is the case with conventional porcelain enamels, proper selection of steel is important also to the most satisfactory application of the high-temperature coatings. In general, single-coat applications can be made on any of the so-called low-carbon steels. In order to prevent blistering in two-coat applications of the *A–31* type, however, the carbon content of the metal should preferably not exceed 0.15 percent.

Coatings of the *A–19* and *A–20* types can be satisfactorily applied on most high-temperature alloys of the austenitic types if the thickness of coating is kept below 0.003 in. The high thermal expansion of these alloys makes the heavier applications impracticable because of the tendency toward chipping due to excessive strains.

2. Preparation of Metal

The metal must be properly cleaned before application of the ceramic coatings if satisfactory results are to be obtained. In general, the metal must be more deeply etched than is common when ordinary porcelain enamel is applied. When feasible, sandblasting is recommended, but satisfactory adherence can be otained by pickling if a suitable procedure is used. Grease must be completely removed prior to pickling, and a heavy nickel flash is imperative even when the steel is cleaned by sandblast. For this purpose a 3-percent solution of nickel-ammonium sulfate heated to 160° F, and with the pH adjusted at 5.2 ± 0.2 with H_2SO_4, or NH_4OH, has been found effective. The recommended time of immersion of the cleaned metal in this solution is 15 minutes.

3. Preparation, Application, and Firing

The method of preparation of the new ceramic coating material is not appreciably different from the methods used for ordinary porcelain enamel ground coat. The frit and other mill batch materials listed in table 3 are introduced into the ball mill and ground to a fineness that will give the desired texture. This will usually require grinding until approximately 1 percent of the weight of the frit will be retained on a No. 200 sieve.[8]

Before removing the slip [9] from the mills, an additional 20 lb of water per 100 lb of frit is added, and the mills are then revolved for a few minutes to mix the added water. Final adjustment of the consistency of the slip is made by adding a solution of either citric acid or sodium pyrophosphate and by adding or drawing off water as needed. The recommended specific gravity is 1.60 to 1.62 for all three slips (table 3), although there is no objection to a somewhat higher or lower specific gravity if the dipping weight falls within the desired limits. The dipping weight for first coats is 0.42 to 0.49 oz (12 to 14 g) of dry enamel per square foot of surface. For second coats it is 0.28 to 0.35 oz (8 to 10 g) per square foot.

Because of the fine grinding (ordinary ground-coat enamels are frequently ground to 6 to 8 percent retained a No. 200 sieve), longer milling periods are necessary. Experience has indicated that this milling time is increased approximately 50 percent over that needed for conventional ground coats.

The coatings may be applied to suitable shapes by spraying, but exhaust stacks and similar items having interior surfaces that require coating, must be dipped. The thickness of the fired coating for one-coat applications should be 0.002 in. to 0.003 in., the intermediate value of 0.0025 in. being sought. Thickness greater than 0.003 in. may be used, but heavier applications reduce thermal-shock resistance and also are more likely to cause such defects as blistering or spontaneous chipping.

The firing temperature for the coatings on ordinary steels is 1,550° to 1,600° F. The time of firing varies with the gage of the steel, the size

[8] Fineness of grinding influences the surface characteristics of the finish produced with the NBS ceramic coatings. When milled so that 2 or 3 percent of the frit is retained on a No. 200 sieve, a rough, full-mat surface results. With finer grinding (0.5 to 1.0 percent retained on a No. 200 sieve) the surface becomes smooth and satinlike. Extremely fine grinding of coating *A–19*, so that only a trace of material remains on a No. 325 sieve, produces a full gloss finish. A coating prepared in this way may be applied in very thin applications and has been designated as *A–19f*.

[9] A slip is defined as the finely ground, creamy water suspension resulting from grinding the mill batch.

and shape of the piece, and the furnace used. For small sample shapes made of 18-gage steel, the proper firing time is 4 to 5 minutes.

V. Service Tests

In the laboratory tests described in section III, wide variations were found in the resistance of the different coatings to the respective treatments. Whether these same coatings would perform similarly when applied to exhaust parts was not known and could be determined only by applying the various coatings to steel exhaust systems and making tests under the conditions of temperature and thermal gradients that exist during engine operation.

By early 1943, a number of exhaust parts had been coated and service tests were under way. By the time the testing program was terminated, a considerable number of sets of exhaust stacks, coated at the National Bureau of Standards, using both conventional enamels and the new ceramic coatings, had been tested by the Philadelphia Naval Air Experiment Station and the Norfolk Naval Air Station (both at the direction of the Navy Department Bureau of Aeronautics), the Army Air Technical Service Command at Wright Field, the Bell Aircraft Corp., and the Glenn L. Martin Co.

Collector-type exhaust systems also were coated. These were tested by the Army Ordnance Tank Automotive Center, the Navy Department Bureau of Aeronautics, the Aeronca Aircraft Corp., and the Grumman Aircraft Engineering Corp.

1. Exhaust Stacks

One of the first sets of exhaust stacks to be tested is illustrated in figure 7. This shows the condition of the stacks after 178 hrs of block-test operation on a 1,350-hp XR–1820–56 Wright radial motor. Coating *A–31* shows no effect from the treatment, whereas the *C–9*, *C–1*, and *C–8* coatings show the same type of defects noted earlier in the laboratory tests. The relative degree of damage follows the order that would be predicted from the flame-impingement and thermal-shock tests.

Two types of defects are present on the damaged stacks. One is a series of cracks following a design apparently corresponding to the strain lines caused by temperature gradients. The other defect consists of the formation of blisters of the type known in the enamel industry as "reboil." These eventually broke, leaving exposed metal beneath. Such blisters have a tendency to segregate along the cracks formed by thermal strains, whereas in other areas where no cracks are formed, they are scattered and show no definite pattern. These distributions correspond to those found in laboratory tests on flat specimens, as illustrated in figure 3.

Figure 8 shows two Glenn L. Martin No. 279303 stacks after 300 flying hours on a PBM–3D patrol bomber operating out of Norfolk, Va. The *A–31* stack (on the left), which has an average coating thickness of 0.004 in., is not visibly affected by this treatment. The stack on the right, coated with *C–1* in an average thickness of 0.0035 in., shows numerous broken blisters and cracks with serious rusting taking place at the discontinuities in the coating. The other service tests made on coated steel exhaust systems also, without exception, showed the newly developed coatings to be superior to the conventional glossy types. In no case did the *A–19* or *A–31* coating show either cracks or reboiling.

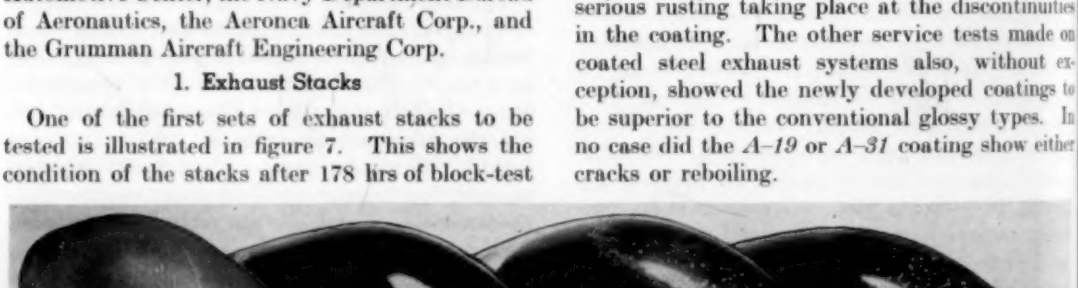

FIGURE 7.—*Four coated steel exhaust stacks after 178 hours of block-test operation on a 1,350-hp radial motor at the Naval Air Experiment Station, Philadelphia, Pa.*

Coating *A-31* is one of the heat-resisting compositions developed at the National Bureau of Standards; *C-9*, *C-1*, and *C-8* are three commercial coatings submitted for test.

FIGURE 8.—*Coated steel exhaust stacks tested simultaneously for 300 flying hours on a PBM–3D patrol bomber at Norfolk Naval Air Base.*

Stack on left is protected with the NBS ceramic coating *A–31* and is unmaged, whereas the stack on right, which is coated with commercial amel *C–1* shows scattered broken blisters, serious rusting taking place at e resulting breaks in the coating.

Some cracking of the metal was observed in ervice tests of stacks, especially those sharply urved near the inlets, and it was noted that steel aving carbon contents in the range 0.10 to 0.25 ercent were more resistant to such failure than as ingot iron. This observation was in agreeent with the results of laboratory tests on nbrittlement, given in table 9.

NBS coatings *A–19* and *A–31* gave adequate rotection to the steel, but because *A–19* is a one-oat application, whereas *A–31* requires two coats, e *A–19* was recommended for exhaust-stack pplications. Where metal temperatures near ,250° F or somewhat above are encountered, *A–31* is recommended in preference to *A–19*, but he strength properties of low-carbon steels are so ow in this temperature range that the number of possible applications is limited. With special steels having better high-temperature strength, higher operating temperatures of coated stacks might be possible.

2. Exhaust Collector Systems

Tests made on collector parts for aircraft motors gave results similar to those obtained on stacks. The *A–19* and *A–31* types again merited superior ratings when they were tested in direct comparison with the conventional glossy coatings.

Figure 9 shows sections from two of a series of coated collector rings tested under the supervision of the Tank Automotive Center of the Detroit Ordnance District of the Army Service Forces. These parts were tested on a 9-cylinder 450-hp Continental Motor of the type used on the M–4 tank. The part on the left was coated with *A–31* and had been on the motor for 120 hr of dynamometer operation. The other coating, which was one of the poorest tested, was a proprietary product of the glossy type applied by the manufacturer and had been under test for 13.5 hr, or only about one-tenth as long as the part coated with *A–31*. Except for a yellowish-brown deposit that accumulated during test, and which could be

FIGURE 9.—*Sections of coated steel collector rings after operation on a 450-hp, 9-cylinder Continental motor undergoing dynamometer tests.*

The part on the right, which was protected with one of the poorest conventional enamel coatings, has undergone 13.5 hr of test and shows pronounced chipping and cracking of the coating. The part on the left is protected with NBS ceramic coating *A–31* and has undergone 120 hr of testing without cracking or reboiling. The area within the circle was cleaned of grease and other external deposits, showing the undamaged coating beneath.

readily removed by scouring [10] there was no visible evidence of change in the *A–31* coating. The glossy coating, on the other hand, shows serious cracking and chipping along certain strain lines with exposed metal appearing at the base of the damaged areas.

Proving-ground tests were made on 10 collector rings installed in tanks. One of these collector rings was coated with *A–19* at the National Bureau of Standards, and the others were coated by seven enamel-frit manufacturers to whom the uncoated collector rings had been submitted by the Tank Automotive Center for application of coatings recommended by these manufacturers. After about 2,500 miles of operation on M–4 tanks only the *A–19* coating received an excellent rating. The other coatings, without exception, showed damage, most of which consisted of thermal cracks and blisters.

Tests on other exhaust collector parts also showed the newly developed coatings to be superior. One finding in this part of the work was that the high-temperature strength of low-carbon steel is not sufficiently good to make the use of such steel feasible for the large collector rings on the more powerful motors, such as the 2,000-hp Wright radial motor. Two collector rings were coated for trial in this type of installation and failed in only a few hours of operation. These collectors operate above a red heat, and the low-carbon steel apparently does not have sufficient strength to withstand this service, and the coating does not add materially to this strength.

VI. Specifications for High-Temperature Coatings

The performance of the high-temperature ceramic coatings in both laboratory and service tests led to the preparation of appropriate specifications. These were issued as Army-Navy Aeronautical Specification AN–C–133 and as tentative specification AXS 1449 of the Army Ordnance Department. The principal requirements as written into these specifications are as follows:

(a) *Thermal-Shock Resistance.*—The coating must withstand five quenches from a temperature of 1,200° F without visible damage, heat being supplied continuously to the underside of the quenched area. This test is performed on two coated, 18-gage tubes 6 in. long and 2½ in. in diameter, or on a section of exhaust tubing. A modified Meeker-type burner with a 90-degree elbow fitted onto the burner end is inserted into the test cylinder. The flame is lighted, and the burner is adjusted so that the temperature of the test area (as measured by a base-metal thermocouple with each wire welded separately to the outside of the steel tube) will pass through the temperature zone 1,185° to 1,215° F in 30 seconds. The flame is then extinguished and relighted. When the temperature again reaches 1,200° F, 25 ml of water at 70°±10° F is allowed to flow freely from the unconstricted large end of a 25-ml pipette onto the heated area of the cylinder between the thermocouple welds. This treatment quickly cools the affected area to a temperature below 212° F, as can be seen from the fact that before all of the water has left the pipette the surface of the specimen sustains a film of water instead of instantly vaporizing it as at the beginning of the quenching treatment. When the temperature again reaches 1,200° F, the quench is repeated until a total of five cycles has been accumulated.

(b) *Oxidation Resistance.*—The protection of the metal against oxidation must be such that a 2½-in. by 3-in. coated specimen of 18-gage enameling iron shall not gain in weight more than 0.03 g during 48 hr of heating at 1,200° F.

(c) *Thickness of Coating.*—The thickness of coating must be not less than 0.002 in. nor greater than 0.003 in. on principal areas nor greater than 0.006 in. at beads.

VII. Production of Coated Exhaust Parts

Commercial production of low-carbon-steel exhaust stacks with NBS ceramic coating *A–19* was started in 1944. By the end of the war, three enameling companies had applied the coating to aircraft exhaust stacks in substantial quantities. As the shortage of stainless steel never became so acute as to restrict its use in aircraft, the *A–19* coating on low-carbon steel was used through preference rather than through an enforced substitution.

Another application of the *A–19* coating that reached the production stage before the end of the

[10] Chemical analysis of the deposit revealed that lead was the principal constituent, comprising 72 percent of the inside and 44 percent of the outside deposit. The source of this lead must have been from the leaded fuel, leaky connectors being responsible for its presence on the outside surface of the collector ring. No carbon or iron was detected in either the inside or outside deposit.

war was the coating of tail pipes for the exhaust systems of the amphibious truck, or "DUC". One section of this pipe was 9 ft long by 1¾-in. in inside diameter, with S-shaped curves at each end. Two other sections were approximately 3 ft and 2 ft long, respectively, with 2½-in. inside diameters. It is considered significant that the coating could be applied satisfactorily to such complex shapes. These pipes were originally fabricated of uncoated low-carbon steel and failed rapidly in service, through corrosion. Not only high operating temperatures, but also proximity to, and contact with, ocean water contributed to the corrosion. Tests showed that coating *A–19* provided satisfactory protection.

VIII. Potential Uses of Coatings

In addition to the use of the new coatings for the protection of low-carbon steel in various military exhaust systems, there are a number of other possible applications where the new coatings, or modifications thereof, might be beneficial in prolonging the life of steel parts that are subjected to relatively severe temperature conditions. A list of such potential applications would include the following: (1) Domestic stove parts, such as grates or burners, (2) industrial furnace parts, such as muffles, dampers, or burners, (3) parts for heat interchangers, (4) heat baffles for continuous enameling furnaces, (5) annealing boxes, and (6) mufflers and tail pipes for buses, trucks, and automobiles.

IX. Summary

A new type of ceramic coating for the protection of mild steels in high-temperature service was developed during the war at the National Bureau of Standards, and was used by the Army and Navy on the exhaust systems of certain aircraft and other vehicles. Laboratory and service tests have shown these new coatings to be superior to conventional porcelain enamels for high-temperature service. The outstanding features of the coatings are (a) high resistance to chipping under repeated severe thermal shock, (b) protection of the metal against oxidation during prolonged exposure in air at temperatures up to about 1,250° F, (c) freedom from the cracking and blistering produced in conventional porcelain enamels under comparable conditions of high temperatures and severe thermal gradients, and (d) a mat surface that does not show highlights and, therefore, decreases the visibility.

To prepare these coatings, a mixture of a special grade of calcined aluminum oxide and a conventional type of ground-coat frit is ground with water to appropriate fineness and is then applied to the metal, dried, and fired according to well-known methods. The coatings may be used on low-carbon steel in an unprecedently thin application of only 0.002 to 0.003 in.

Specifications were issued by the armed services, and the coating was used in regular production during the war on a number of exhaust parts by both the Army and Navy.

Modifications of these ceramic coatings are possible and may find a use for lower temperature applications.

The development of the new type of coating through the stages of laboratory study, service tests, and regular production was made possible by the cooperation of several agencies. The Navy Bureau of Aeronautics, Army Air Forces, and, Army Ordnance Department participated in the service testing of the new coatings in parallel with conventional types submitted by manufacturers. Several of the manufacturers and the Porcelain Enamel Institute were instrumental in promoting the use of porcelain enameled exhaust systems and participated in arrangements for some of the comparative tests, especially by the Tank Automotive Center. In addition, a number of aircraft companies cooperated by making extensive tests of the new NBS coatings in direct comparison with conventional porcelain enamels.

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Electrical Characteristics of Quartz-Crystal Units and Their Measurement

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The problem of measuring the dynamic electrical characteristics of high frequency quartz-crystal units was investigated by using ordinary laboratory instruments such as *r-f* bridges and *Q* meters. Measurement methods and technics are given, together with relative merits and limitations. Antiresonance impedance up to 5,000,000 ohms was measured to ±5 percent or better. Data concerning constancy of electrical characteristics, secondary responses, and changes with amplitude of vibration and temperature are given for a large number of 8.7 *Mc BT*-cut crystal units having representative types of mountings. Results obtained on a few 50- and 100-kc units are also included. A convenient type of graphical representation of electrical characteristics of normal crystal units is suggested.

I. Introduction

uring the past few years, emergency demands quartz-crystal units were enormous. Many methods of production, measurement, and were intensively studied and used. Precise surement of the characteristics of each crystal was made; however, data concerning the amic electric impedance were mostly sup- in an arbitrary manner [1, 2].[1]

he problem of measuring a crystal unit as , i. e., without the use of a particular type of llator, was presented by the Army Signal ps to the Bureau and several other laborator- The results given in this paper supplement e obtained by others [3, 4] and lead to more rt methods of rating performance and of ifying, measuring, and standardizing those meters likely to be most useful to the radio electronics engineer.

A quartz-crystal unit may be precisely speci- and measured apart from any external speci- s with which it is used. This has been proved various occasions in print and in discussion 5, 7]. This paper reviews ways of expressing equivalent electric circuit and describes surement methods and technics by which may determine the electrical characteristics a crystal unit over a wide range of frequency and impedance, with such commonly used equipment as r-f bridges and *Q*-meters; it shows how one may present the performance characteristics in a simple way to assist in differentiating between a normal unit and one remaining constant only under a limited set of conditions.

The "activity" of a crystal unit is sometimes defined in terms of both grid current and speed with which oscillations start and stop when a test oscillator is keyed. Certain applications of crystal units require data concerning electrical, mechanical, and thermal transients. Such data, including overload or burnout-characteristics, are not dealt with in this paper. However, they may be associated with and supplement any desirable steady state index of performance.

The measurement methods described were useful in exploring nearby or overlapping secondary responses and regions above and below the maximum antiresonance frequency of the crystal unit. Constancy of electrical characteristics from day to day and changes with temperature and amplitude of vibration were investigated for a large number of 8.7-Mc, BT-cut units having representative types of mountings. Changes in the fundamental electrical equivalent characteristics were not observed in selected units at crystal currents up to about 100 ma. Data concerning the foregoing are presented in graphical form. Results obtained on a few 50- and 100-kc units, having metal-film electrodes, are also given.

[1] Figures in brackets indicate the literature references at the end of this paper.

II. Equivalent Circuit Representing A Normal Mode of Vibration

Piezoelectric crystals were introduced into the radio-frequency field to meet the need for a resonant circuit (either series or parallel) having constant parameters and low losses (high Q). A fundamental requirement in this application was therefore that the quartz-crystal unit be the electrical equivalent of a single resonant (or antiresonant) circuit. The unit that most nearly meets this requirement may be referred to as a normal crystal. Other units having interfering responses, or closely spaced multiple resonances, are apparently equivalent to electric-circuit meshes having a number of mutually coupled resonant circuits. These may be treated as complex crystals and should be dealt with separately.

It should be pointed out, however, that this differentiation between "normal" and "complex" crystal units applies to the major mode of vibration of a crystal unit and to the responses that may be immediately next to it.

The equivalent circuit of a normal crystal is shown in figure 1, a. It has one resonant (f_r) and one antiresonant (f_a) frequency. The impedance across its terminals may well be illustrated by means of the susceptance and reactance diagrams shown in figure 1, c and d. R_s is small compared with ωL and can be neglected in these diagrams.

The susceptance (B_{abc}) of the L_1, C_1 series branch is added to the susceptance (B_t) of the shunt capacity C_t. C_t is the total shunt capacity across the crystal and is usually designated as C_0 when the external capacity is zero. The resultant B_e is obtained in figure 1, c as the resultant termination reactance X_e in figure 1, d. It is evident from the diagram that as C_t is increased in value the slope of B_t will increase and f_a will approach f_r. It is also apparent that X_e is positive between f_r and f_a. The equivalent circuit at frequencies in this range is therefore as shown in figure 1, b, where R_e is the resistive component, including the effect of the series resistance R_s and all other losses of the unit. When such a circuit is tuned to antiresonance with an external capacitor, the termination impedance is resistive and is equal to

$$R_p = Q_e X_e = \frac{X_e^2}{R_e}. \qquad (1)$$

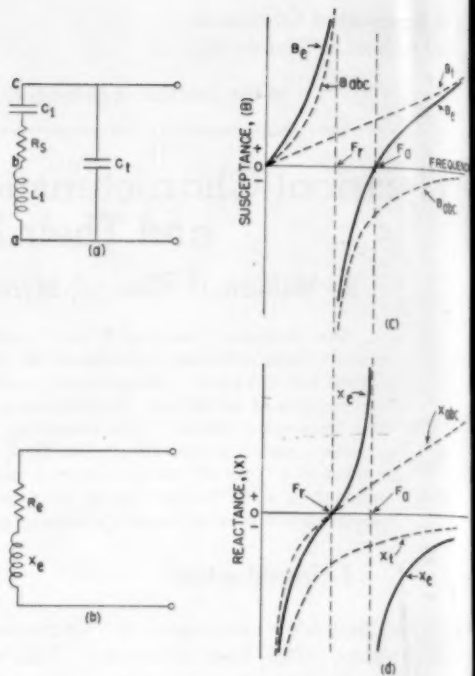


FIGURE 1.—*Electrical equivalents of quartz-crystal u*

a. Equivalent circuit of quartz-crystal unit; *b*, effective impedan quartz-crystal unit between f_r and f_a; *c*, susceptance diagram of a cr unit; *d*, reactance diagram of a crystal unit.

R_p in some literature is referred to as the p formance index (*PI*). The equivalent termi tion impedance of the equivalent circuit of fig 1 may also be expressed in terms of the tun shunt-capacity and the series resistance R_s follows: At any antiresonant frequency, f_a, (whe $f_a > f_r$) the termination impedance is for practi purposes equal to that of a tapped antiresona circuit and is resistive, namely,

$$Z_p = R_p = Z_z \frac{C_1^2}{(C_1+C_t)^2},$$

where

$$Z_z = Q_z \frac{1}{\omega C_e} = \frac{1}{R_s(\omega C_e)^2}.$$

Q_z is the Q of the antiresonant circuit, and $C_e = (C_1 C_t)/(C_1+C_t)$.

$$R_p \doteq \frac{1}{\omega^2 C_t^2 R_s} = \frac{X_t^2}{R_s}.$$

m eq 1 and 2

$$\frac{X_l^2}{R_s} \doteq \frac{X_c^2}{R_c}. \tag{3}$$

R_p may be plotted versus C_t as an independent rameter in the form of a straight line having a gative 2 to 1 slope as shown in figure 4. This llows from eq 2 as

$$\log R_p = \log\left(\frac{1}{\omega^2 R_s}\frac{1}{C_t^2}\right) = \log\frac{1}{\omega^2 R_s} - 2\log C_t.$$

is assumed to be a constant, and the per- ntage change in ω with C_t is assumed to be gligible. These assumptions are justified on basis of experimental evidence, as is shown ewhere. Hence

$$\log R_p = K - 2\log C_t. \tag{4}$$

Similarly, the antiresonant frequency incre- nts $(f_a - f_r)$ may be placed as a straight-line nction of C_t having a negative 45 degree slope, shown in figure 4. This may be shown as llows:

The resonance frequency is given by the relation ee fig. 1, a)

$$\omega_r^2 = \frac{1}{L_1 C_1}. \tag{5}$$

he antiresonance frequency is determined from e interrelation

$$\omega_a^2 = \frac{1}{L\frac{C_1 C_t}{C_1 + C_t}} = \frac{C_1 + C_t}{L_1 C_1 C_t} \tag{6}$$

om 5 and 6

$$\frac{\omega_a^2}{\omega_r^2} = \frac{f_a^2}{f_r^2} = \frac{(C_1 + C_t)C_1}{C_1 C_t} = 1 + \frac{C_1}{C_t} \tag{7}$$

$$\frac{f_a^2}{f_r^2} - 1 = \frac{f_a^2 - f_r^2}{f_r^2} = \frac{C_1}{C_t}. \tag{8}$$

Therefore,

$$\frac{(f_a + f_r)(f_a - f_r)}{f_r^2} = \frac{C_1}{C_t}. \tag{9}$$

or practical purposes, $(f_a + f_r) = 2f_r$. Hence

$$\frac{2(f_a - f_r)}{f_r} \doteq C_1 C_t^{-1}, \tag{10}$$

and

$$(f_a - f_r) \doteq \frac{1}{2} f_r C_1 C_t^{-1} \tag{11}$$

or

$$\log (f_a - f_r) = \log\left(\frac{1}{2} f_r C_1\right) - \log C_t. \tag{12}$$

As f_r and C_1 remain constant,

$$\log (f_a - f_r) = K - \log C_t, \tag{13}$$

and the function of log $(f_a - f_r)$ versus log C_t has a negative slope of 45 degrees.

Measurement results shown later (section IV) demonstrate how closely the straight lines and slopes were reproduced. The advantage of this method of presentation will also be apparent when the resulting curves are studied. A departure from either a straight line or from the proper slope usually indicated abnormally high series resistance or the proximity of an interfering closely coupled mode of vibration. Other information conveyed in this manner will be discussed later.

III. Measurement Methods

1. Parameters Involved

The following parameters were investigated in these measurements:

C_0 = internal capacity of a crystal unit with the crystal inactive.

$C_t = C_0 \pm \Delta C_t$ = total effective capacity shunting the equivalent series resonant circuit of a crystal unit as shown in figure 1, a.

ΔC_t = an increment of C_t

C_1 = equivalent series (motional) capacity as shown in figure 1, a

f_r = series resonance frequency of the crystal unit

f_a = parallel resonance (antiresonance) frequency of the crystal-unit at any C_t.

$\Delta f = f_a - f_r$

L_1 = equivalent series inductance as shown in figure 1, a

R_s = series resistance of the crystal as shown in figure 1, a

R_p = equivalent antiresonance impedance (nonreactive) of the crystal unit corresponding to different values of C_t.

R_c = equivalent series resistance of a crystal unit at any frequency, as shown in figure 1, b

R_h = resistance shunting the quartz crystal (equivalent to holder losses)

$Q_e = \frac{X_e}{R_e}$ = the effective "Q" of the crystal unit

$Q_z = \frac{2\pi f L_1}{R_s} = \frac{1}{2\pi f C_1 R_s}$ by definition, where f is the nominal frequency of the crystal unit. This is usually referred to as the "Q" of the crystal.

X_e = the equivalent series (positive or negative) reactance of the crystal. $X_t = (1/2\pi f C_t)$.

Some useful expressions of parameters in terms of the directly measurable quantities are derived as follows:

From eq 11 above,

$$C_1 \doteq \frac{2\Delta f C_t}{f_r} \tag{14}$$

Substituting this value into the defined expression of Q_z and noting that $\Delta f \ll f_r$; i. e., that any frequency between f_a and f_r can be used for this expression.

$$Q_z = \frac{f_r}{(2\pi f_r)2\Delta f C_t R_s} = \frac{1}{4\pi\Delta f C_t R_s}. \tag{15}$$

Measurements of f_a to determine Δf are usually made at $C_t = C_0$, then

$$Q_z = \frac{1}{4\pi\Delta f C_0 R_s}. \tag{16}$$

At resonance

$$L_1 = \frac{1}{(2\pi f_r)^2 C_1}. \tag{17}$$

Equations 1 and 2 express R_p in terms of C_t and X_e.

The effect of holder losses reduces R_p values to

$$R'_p = \frac{R_h R_p}{R_h + R_p}. \tag{18}$$

2. Q-Meter Measurements

It is noted above that the equivalent circuit of a crystal unit is a reactance X_e in series with a resistance R_e at all frequencies between f_r and f_a. Numerous papers have shown the significance of these parameters in oscillators and filters. These parameters may be measured with laboratory instruments of which the Q-meter, twin-T, and impedance bridge were used here. These will be briefly analyzed.

The well-known Q-meter principle makes use of an antiresonant circuit arrangement, as shown in the table of figure 3.

L_Q, C_Q is tuned for antiresonance at the frequency at which X_e, R_e is to be measured. The crystal unit is then connected across C_Q. It is evident that C_Q has to be readjusted by ΔC_Q to restore the antiresonance at the Q-meter tank and that in general

$$X_e = \frac{1}{\omega(\Delta C_Q)} \tag{19}$$

At f_a of the crystal unit corresponding to $C_t = C$, ΔC_Q will be zero; for lower and higher values of f_a, ΔC_Q will be correspondingly positive and negative.

The voltage across the antiresonance tank is a measure of the Q of the circuit. Connecting the crystal unit across the tank reduces the original Q as a result of the shunt effect of R_e. From the two values of Q, R_e can be computed from

$$R_e = \frac{1.59\times 10^8\left(\frac{C_{Q1}}{C_{Q2}}Q_1 - Q_2\right)}{fC_{Q1}Q_1Q_2}, \tag{20}$$

where

C_{Q1} = the capacity, in micromicrofarads, required to tune the Q-meter tank without the crystal unit at the crystal frequency

C_{Q2} = the capacity, in micromicrofarads, required to tune the Q-meter tank with crystal unit in parallel with it

Q_1 = the original Q of the tank

Q_2 = the reduced Q of the tank

f = the nominal frequency in kc/s of the crystal unit.

The equivalent antiresonant impedance (nonreactive), R_p, of the crystal unit (PI) [6, 7] is the impedance of the crystal unit at a given frequency between f_r and f_a with the proper capacity connected in parallel with it.

The equations below state the values of R_p and R_s directly in terms of the Q's observed.

$$R_p = \frac{1.59\times 10^8 Q_1 Q_2}{fC_{Q_1}(Q_1 - Q_2)} \tag{21}$$

$$R_s = R_p\left[\frac{(Q_1 - Q_2)C_{Q_1}}{Q_1Q_2(C_{Q_2} - C_{Q_1})}\right]^2, \tag{22}$$

where the terms are as stated for eq20.

For high R_p values, corrections are made for holder losses; the corrected R'_p value (from eq18) should then be used in eq22.

Measurements of R_p values down to a few thousand ohms may be made with the Q-meter by using the above formulas. It was found, however, that a direct substitution method of using r-f resistors eliminated time-consuming computations, without sacrificing accuracy.

A number of cpils (from 0.5 to 10 μh for the 8.7 Mc units) were tuned to the desired frequency, and their effective Q's were calibrated against r-f

Figure 2 shows a block diagram of the equipment. For low voltages (across the crystal units) a commercial Q-meter was used. Stable-frequency *r-f* voltage was applied directly to the 0.04 ohm resistance element in the Q-meter tank with the internal oscillator disconnected. This was done by leaving the Q-meter band switch in an intermediate position.

Some of the precautions observed while using the Q-meter are mentioned. Calibration curves were made with the external source, and the resistors and crystal units were connected across

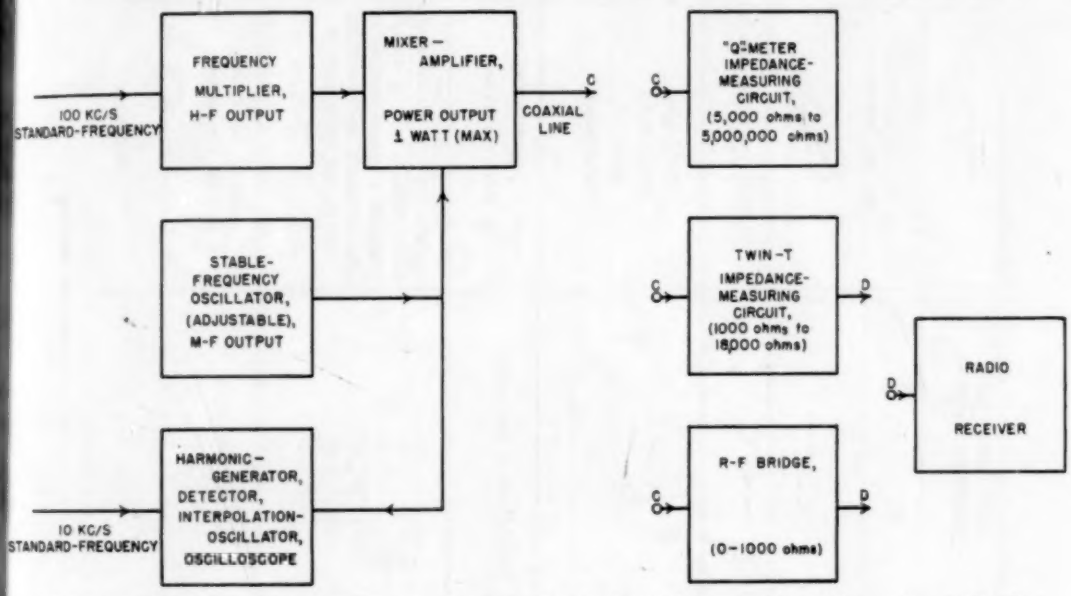


FIGURE 2.— *Block diagram of the apparatus used in measuring the electrical characteristics of the quartz-crystal units.*

resistors. The resistance values of the latter were checked from time to time with a d-c resistance bridge. These resistors were of the metallized-filament type enclosed in an isolantite body. The discrepancy between the *d-c* and *r-f* values of these resistances and the degree with which the Q-meter values can be read and reproduced largely determine the accuracy of these Q-meter measurements. Conservative estimates of the over-all accuracy are tabulated in figure 3. The inductance and the Q of an individual coil determine its resistance range for greatest accuracy; this is readily apparent when calibration curves of R_p's are plotted against Q_2 on semilog paper with resistance on the logarithmic coordinate.

the Q-meter tank with shortest leads practicable. Care was taken to eliminate all direct pick-up in the coils. Plug-in arrangements were such that no additional losses were introduced across the crystal units. Inaccuracies in measurements as a result of Q-meter limitations were often checked. Among these was the effect of the "Q" level on values of C_0 usually measured with the Q-meter (using the internal oscillator at a frequency considerably below the nominal crystal frequency). The current level in the 0.04-ohm resistor was maintained constant for a given zero setting of the "Q"-indicator. Values of external capacitors used as ΔC_t were measured at the nominal frequency of the crystal units.

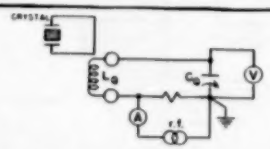
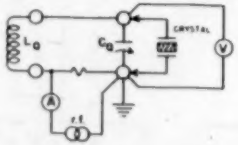
PARAMETER	RANGE	INSTRUMENT	CIRCUIT ARRANGEMENT (FUNDAMENTAL SCHEMATIC)	PROCEDURE	PRECAUTIONS	ACCURACY, CONSERVATIVE ESTIMATE
STATIC CAPACITY C_0, AND PARALLELING CAPACITY ΔC_t	0 TO 30 $\mu\mu f$	"Q" METER	SEE f_s	CALIBRATE C_0 VS. DIAL SETTING. $C_0 = C_{0_1} - C_{0_2}$	MEASURE C_0 AT r.f. FOR WHICH CRYSTAL IS INACTIVE. POSITION AND SHIELDING OF CRYSTAL UNIT IS IMPORTANT	± 0.1 $\mu\mu f$
	30 TO 150 $\mu\mu f$					± 0.2 $\mu\mu f$
	150 TO 2000 $\mu\mu f$					± 5 $\mu\mu f$
	100 TO 1100 $\mu\mu f$	TWIN-T IMPEDANCE-MEASURING CIRCUIT	SEE R_p	CALIBRATE CAPACITANCE DIAL		± 2 $\mu\mu f$
SERIES-RESONANCE FREQUENCY, f_s	"Q" METER	"Q" METER		ADJUST L_0C_0 FOR MAXIMUM V. ADJUST r.f. FOR MINIMUM V.	USE SHORTED TERMINALS OR SMALLEST LOOP FOR INDUCTIVE COUPLING TO CRYSTAL UNIT	± 1.5 IN 10^6
	R-F BRIDGE	R-F BRIDGE	SEE R_s AND R_s (HIGH LEVEL)	ADJUST r. f., AND RESISTANCE ARM OF BRIDGE FOR BALANCE	SHIELD WELL. NO F.M. IN OUTPUT OF r-f GENERATOR	± 1.5 IN 10^6
ANTIRESONANCE FREQUENCY, f_a	"Q" METER	"Q" METER		TUNE "Q" METER TO f_s. PLACE CRYSTAL UNIT IN PARALLEL WITH C_0. INCREASE r.f. FOR MAX. V. REMOVE CRYSTAL UNIT AND RETUNE "Q" METER. REPLACE CRYSTAL UNIT AND READJUST r.f. FOR MAX. V.	FOR MAXIMUM PRECISION ADJUST C_0 FOR MAX. V. USE LARGE L/C RATIO IN "Q" METER	± 2.5 IN 10^6
	TWIN-T CIRCUIT	TWIN-T CIRCUIT	SEE R_p (LOW LEVEL)	ADJUST r. f., AND C_0 ARM OF BRIDGE FOR BALANCE	SHIELD WELL	± 2.5 IN 10^6
EQUIVALENT SERIES RESISTANCE R_s, AND REACTANCE, X_s	0 TO 1000 OHMS	R-F BRIDGE	SEE R_s	ROUTINE	SHIELD WELL. USE LOW r-f INPUT TO BRIDGE	± 0.2 OHMS ± 2%
	0 TO 500 OHMS (AT 10 Mc)					± 1 OHM ± 1%

FIGURE 3.—*Outline of measurement methods used.*

FIGURE 3.—*Outline of measurement methods used.*

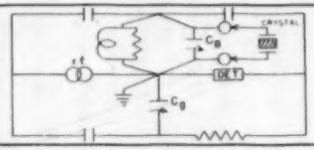
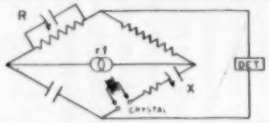
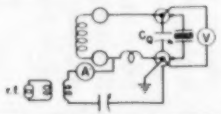
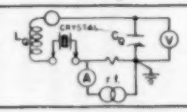
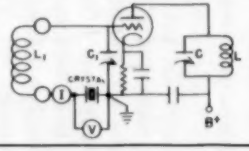
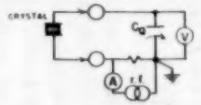
ANTIRESONANCE IMPEDANCE, R_p (LOW LEVEL)	5000 TO 10,000 OHMS	"Q" METER	SEE f_a	SUBSTITUTION METHOD. ADJUST r.f. FOR MAXIMUM V. AT EACH ΔC_t	FOR MAXIMUM PRECISION ADJUST C_0 FOR MAX. V.	± 5% OR BETTER
	10,000 TO 100,000 OHMS					± 2%
	100,000 TO 5,000,000 OHMS					± 5% OR BETTER
	1000 TO 18,000 OHMS	TWIN-T CIRCUIT		ROUTINE	SHIELD WELL USE LOW r-f INPUT TO BRIDGE	± 2.5 %
	0 TO 1000 OHMS	R-F BRIDGE		ADJUST r.f., AND RESISTANCE ARM OF BRIDGE FOR BALANCE WITH CALIBRATED SILVER-MICA CONDENSERS IN PARALLEL WITH CRYSTAL UNIT	SHIELD WELL USE LOW r-f INPUT TO BRIDGE. NO F.M. IN OUTPUT OF r-f GENERATOR	± 0.1 OHMS ± 1.5 %
R_p (HIGH LEVEL)	1000 TO 100,000 OHMS	SPECIAL HIGH LEVEL "Q" METER		SUBSTITUTION METHOD USE 1 TO 5 WATT r-f INPUT	PERMIT CRYSTAL UNIT TO REACH TEMPERATURE EQUILIBRIUM	± 5 %
SERIES-RESONANCE RESISTANCE, R_s	0 TO 1000 OHMS	R-F BRIDGE	SEE R_p (LOW LEVEL)	SEE f_r	SEE f_r	± 0.1 OHM ± 1 %
	1000 TO 10,000 OHMS	"Q" METER	SEE f_a	SUBSTITUTION METHOD	USE GOOD L_0 COILS AND LOW L_0/C_0 RATIOS	± 5%
	0 TO 10 OHMS			SUBSTITUTION METHOD		± 2.5 %
R_s AND f_r (HIGH LEVEL)	0 TO 100 OHMS AND ABOVE	SPECIAL CIRCUIT ARRANGEMENT		ADJUST L,C FOR MAXIMUM I, AND E_p FOR DESIRED I VALUE. ADJUST C_1 FOR MINIMUM V. $R_s = \frac{V}{I}$	CALIBRATE I AND V SEE R_p (HIGH LEVEL)	NOT FULLY INVESTIGATED
R_p	5,000 TO 5,000,000 OHMS	"Q" METER WITH LOW C_0		ADJUST r.f. FOR MAXIMUM V. AT A VALUE HIGHER THAN f_r $R = \frac{Q}{\omega C_0}$	V IS MAXIMUM WHEN $C_0 = C_0$ AND FREQUENCY = $f_r + \frac{\Delta f}{2}$	NOT FULLY INVESTIGATED

FIGURE 3.—*Outline of measurement methods used.*

The resonance and antiresonance frequencies (f_r and f_a) were most readily determined with the Q-meter. An unshielded coil was resonated in the Q-meter at a frequency near that of the crystal unit. The crystal unit was short-circuited and placed near the low voltage end of the coil. When the Q-meter frequency was then varied, a sharp dip appeared on the Q-indicator at that frequency equal to the f_r of the crystal unit. As the value of f_r is affected by any inductance or capacitance connected in the short-circuiting path, precautions were taken to minimize this in precise measurements.

Measurements of f_a, (when $C_t=C_0$), were made with the crystal unit connected in parallel with the Q-meter coil. The coil was first resonated at the nominal crystal-unit frequency. After the insertion of the crystal unit, the frequency was varied until the Q-indicator rose to a maximum. With the crystal unit again removed, the coil was resonated at constant frequency by adjusting the variable capacitor (C_Q) of the Q-meter. Once again the crystal unit was placed in the circuit and the frequency adjusted to a maximum Q indication. These adjustments were repeated until a constant, frequency value (f_a) was obtained. At this point $C_t=C_0$.

To measure f_a when C_t is not equal to C_0, the Q-meter capacitance was changed from the $C_t=C_0$ setting by the required ΔC, and the frequency was varied to a new f_a, as indicated by the peaking of the Q-indicator. It is evident that the sharpness of the f_r and f_a indications depends upon the L/C ratio of the Q-meter tank.

Measurements of R_p values corresponding to given frequencies within a response were made by using the substitution method. For highest precision, a final adjustment of C_Q to a maximum Q indication was made at constant frequency. Measured Q values were converted into corresponding R_p values from the R_p versus Q_2 calibration curves. R_p was computed from C_t and R_s, for R_p values low enough to be unaffected by holder losses.

Values of R_p at voltages closely approaching those applied to the crystal unit in a Miller- (or Pierce-) type oscillator were determined with the specially constructed circuit shown in figure 3. This circuit was similar to that of the Q-meter, except that the voltage was injected into the L–C tank by link-coupling the output of an auxiliary amplifier into a very small section of the tank inductance. The substitution method was again used. The current- and Q-indicators of the regular Q-meter were replaced by sensitive thermoelements with potentiometer-indicators. Great care had to be observed in these measurements to avoid the frequency response shift, as the temperature of the crystal unit varied with the high current through it. The procedure was modified to enable presetting the voltage values. desired. Since, as is shown below, there was no apparent difference in the R_p values at high and low voltages, there seems to be no need of measuring crystal parameters at high voltages. The procedure is therefore not elaborated upon.

The Q-meter was used for measurements of R_s values directly. The crystal units were connected in series with the tank coil for low values of R_s (up to 10 ohms) and in parallel with the tank for values higher than 1,000 ohms. It was found, however, that an r-f impedance bridge was more suitable for measurement of R_s values from 1 to 1,000 ohms. This is described later in greater detail.

It should be mentioned here that when a crystal unit is connected across a tank tuned approximately to the crystal frequency there are present two antiresonance peaks of the circuit impedance [5]. As the lower peak is not governed by the frequency response of the crystal unit, and as it appears at a separation many times the width of Δf, it does not affect the method of measurement.

3. Twin-T Circuit and Impedance Bridge

A twin-T admittance measuring circuit was used for R_p values of 1,000 to 10,000 ohms. As this is an admittance measuring device, individual resistance values were computed from the results obtained and were occasionally checked against measurements of carbon-film resistors. Care was taken that increments of C_t applied across the crystal units (either by varying the internal capacity of the instrument or by connecting external condensers across them) were known to the greatest accuracy at the operating frequency. The fundamental circuit is similar to that of the Q-meter and the over-all accuracies were the same as with the Q-meter.

It is possible to measure X_s and R_s values of a crystal unit directly with the twin-T. However, the relatively limited range of the measurable X_s

at corresponding R_e values renders the instrument useful only in double-checking a few points obtainable with the Q-meter, and its use yields little additional information.

A commercial *r-f* bridge was used to measure R_p, R_e and X_e values from 1,000 down to a few ohms, and R_p values down to 100 ohms. In fact, R_p values as low as 10 ohms were actually measured with the 8.7-Mc crystal units. However, the validity of the latter was questioned.

The major requirement in the application of the twin-T and impedance bridge was a stable frequency source, adjustable in small increments of frequency. With such a source and the usual precautions for proper shielding and grounding of the measuring and detecting equipment, no difficulties were encountered in following the normal bridge operation procedures. A source of radio frequency having good waveform without frequency modulation was found essential for a sharp null balance.

The general procedure in measuring R_s and R_p with the *r-f* bridge was to vary the frequency and the resistance arms until a minimum deflection on the null balance indicator was obtained. The value of R_s was measured more rapidly by first determining f_r with the Q-meter, as explained above.

R_p values were measured with external capacitors connected in shunt with the crystal-unit terminals. R_e and X_e values were obtained at any frequency by adjusting the resistance and reactance arms for a null balance.

It was found advisable to use the lowest input voltage to the bridge required for effective operation of the detector. At low-input levels no appreciable heat was generated inside the crystal. Consequently, frequency drift was minimized. Good correlation was then obtained between parameters and frequency values within a given Δf.

The accuracy of the *r-f* bridge in all measurements is shown in figure 3.

4. Secondary Responses

The adjustable frequency range available at the time to explore the spectrum for secondary (spurious) responses limited these measurements to the 8.7-Mc crystal units within a band of 8650 to 8892.5 kc/s. This range is in the process of being extended for wider investigation in the future.

In locating and measuring secondary responses the Q-meter was singularly useful. The Q-meter tank was tuned to a frequency somewhat lower than the nominal frequency of the crystal unit. The frequency was then continuously increased, with the crystal connected across the tank. Voltage dips were then observed at f_r points and peaks at f_a points in the frequency spectrum. Individual responses were closely explored by retuning the tank (with crystal unit removed) and repeating the sweep of frequency to determine more exactly the values of f_r and f_a. The process of retuning the tank and of readjusting the frequency was repeated until no differences in frequency values of f_r or of f_a were noticed.

High-inductance tank coils were more effective in locating f_a values; similarly, low-inductance coils were more effective in locating f_r values. It was sufficient in most cases to use a coil of medium inductance to serve both purposes. For most accurate measurements of the frequencies and equivalent R_p or R_s values, different coils were used as conditions warranted.

It was found convenient and enlightening to plot the relative position of the secondary responses, as shown in figures 8 and 14. For practical purposes it might be sufficient to interconnect the R_s and R_p values of each response with a straight line as the curvature involved is negligible relative to the frequency scale employed. This approximation may be justified analytically when considering the variation of R_e within a single response, between f_r and f_a. Designating the total series reactance of the equivalent circuit of figure 1, a, as

$$X_1=\omega L_1-\frac{1}{\omega C_1} \text{ and } X_0=\frac{1}{\omega C_0},$$

the termination impedance of the unit is

$$Z=X_0\left[\frac{X_0R_s+j[R_s^2+X_1(X_1+X_0)]}{R_s^2+(X_1+X_0)^2}\right], \quad (23)$$

then

$$|Z|=X_0\frac{(X_0^2R_s^2+[R_s^2+X_1(X_1+X_0)]^2)^{\frac{1}{2}}}{R_s^2+(X_1+X_0)^2}. \quad (24)$$

The equivalent series values of R_e and X_e are then

$$R_e=\frac{X_0^2R_s}{R_s^2+(X_1+X_0)^2} \quad (25)$$

$$X_e=\frac{X_0[R_s^2+X_1(X_1+X_0)]}{R_s^2+(X_1+X_0)^2}. \quad (26)$$

For practical purposes, at f_a the reactive component of Z vanishes and $X_1+X_0=0$. Therefore,

$$Z_a \doteq R_p \doteq \frac{X_0^2 R_s}{R_s^2} = \frac{X_0^2}{R_s} \doteq R'_s, \tag{27}$$

where R'_s is the value of R_s at f_a. At f_r, $X_1=0$ and

$$|Z| = X_0 \frac{[X_0^2 R_s^2 + R_s^4]^{\frac{1}{2}}}{R_s^2 + X_0^2} = \frac{X_0 R_s}{\sqrt{X_0^2 + R_s^2}}. \tag{28}$$

For values of $X_0 \gg R_s$,

$$|Z| \doteq R_s.$$

Similarly, at f_r, $X_1=0$, and from eq. 25,

$$R_r = \frac{X_0^2 R_s}{R_s^2 + X_0^2} \doteq R_s.$$

It is therefore apparent that for responses having series-resistance values considerably lower than X_0, plotting R_r versus frequency, as shown in figures 8, 14, and 22, would closely represent a quantitative variation of a single parameter of a crystal unit within the limit of R_s and R_p. For responses having high series-resistance values, this presentation of a response is correct only at the R_p and R_s points. The intermediate points have qualitative significance only. It should be pointed out, however, that the R_p and R_s values representing the top and bottom points of each response are the actual measured values of these parameters. The Q-meter was used to locate the response, and R_s and R_p values were then measured with Q-meter, twin-T, or r-f bridge, depending on the magnitude of the parameter. The initial balance of the bridge and of the twin-T circuit had to be made at the frequency and at the chosen voltage input value of the measurement performed at the time. Not all the relatively small secondary responses (having R_s values above approximately 1,000 ohms) behave alike. Some of these appear to have R_p values considerably lower than their R_s values. Further study of their behavior will be required. Their presence is therefore indicated by a single point representing measured R_s values. One may also assume that the small responses barely detectable with the Q-meter may be neglected.

5. Notes on Methods and Equipment Employed

The equipment shown in figure 2 was used for 8.7-Mc crystal measurements. A standard frequency of 100 kc was fed into a frequency multiplier, the products of which were mixed with the output of a continuously adjustable stable-frequency oscillator. The output of the mixer was then amplified to the desired level.

Frequency could be easily adjusted, measured, and maintained to better than 5 parts in 10 million over a period required to make any one measurement. Regular frequency measuring equipment incorporating a radio receiver as a detector, a stable radio-frequency oscillator to determine the beat frequency between the adjustable oscillator and a harmonic of the standard source, and an oscilloscope were used throughout these measurements. A second radio receiver was used as a null indicator with the twin-T and r-f bridge.

Equipment employed in the measurements of the 50- and 100-kc crystals was essentially the same.

Special circuits were developed and satisfactorily used to measure independently and directly the values of R_s and f_r. For convenient reference, figure 3 outlines briefly the methods, accuracy, and range of parameters measured.

IV. Graphical Presentation and Results of Measurements

1. Characteristics of Normal-Crystal Unit

A crystal unit operating at a frequency response with proper slopes of R_p and f versus C_t is designated as a normal crystal. Figures 4 to 11 show characteristics of normal crystal units. Slopes of 2:1 and 1:1 were plotted for the straight-line sections in figures 4 to 7. The position of the points show the departure of measurement data from the theoretical slopes. Curvatures at high R_p values were caused by holder losses, as evidenced by some of these characteristics measured with the crystal removed from the holders or when placed in low-loss holders. The very low R_p region at these crystal units was not fully investigated.

The displacement of the R_p-C_t curve shown in figure 5 indicates a drop in the R_p values over the entire range of C_t. This apparently resulted from an increased R_s value because of an accumulation of additional dust particles on the crystal plate when it was removed from the holder. It is seen, however, that a 2:1 slope is maintained throughout the curve up to C_t-C_0.

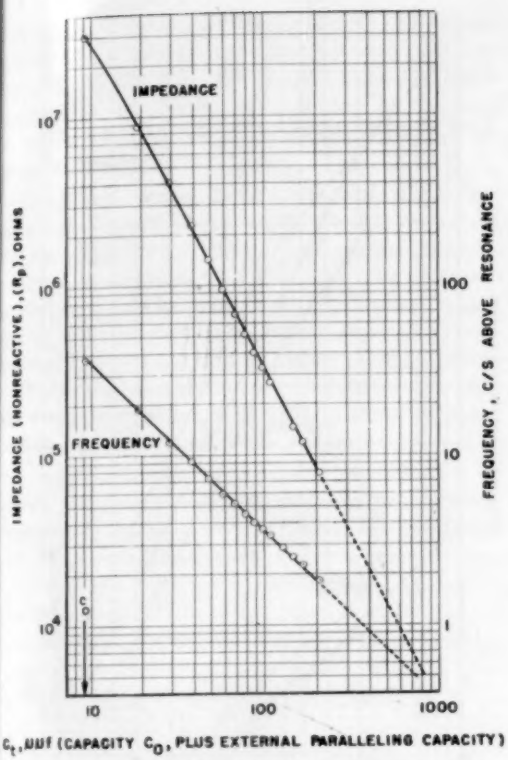


FIGURE 4.—*Electrical characteristics of a 50-kc quartz bar: X-cut, metal-film electrodes, clamp-type mounting.*

Figure 6 shows these characteristics for two plated wire-supported BT-cut 8.7-Mc units. Curves of four other units of the same type were obtained, and, if plotted, would fall between these two sets of curves. A wider variation of R_p values is shown in figure 7, which represents three unplated and one plated pressure-mounted, BT-cut, 8.7-Mc units. The R_p and frequency points of two of the unplated units fall within the curve *A*. The frequency curves of the unplated units deflect from a 45-degree slope as C_1 approaches C_o. It is felt, however, that this may not constitute a real departure from the normal condition. Further investigation should answer this question.

The frequency spectrum of one of the wire-mounted 8.7-Mc units is shown in figure 8. It closely represents the spectrum of every one of this group of six units, both in relative position and in the intensity of the responses. This spectrum shows at a glance the relative freedom of the lowest frequency response from neighboring interfering responses, and should be compared with the spectrum of an unplated unit shown in figure 14.

It seems that two sets of curves similar to those shown in figures 6 and 8 may effectively demonstrate the electrical characteristics and behavior of a crystal unit. This might be more apparent when the curves are compared with those obtained for complex units shown later.

It might seem, at first, as if a single point on the R_p-f-C_1 curve through with the engineer could draw the appropriate 2:1 or 1:1 line would convey sufficient data for design purposes. However, the complete R_p-f-C_1 curves are necessary to show the effect of holder losses, and the actual deviation of the slopes from normal (whatever the cause); while the frequency spectrum is required to show

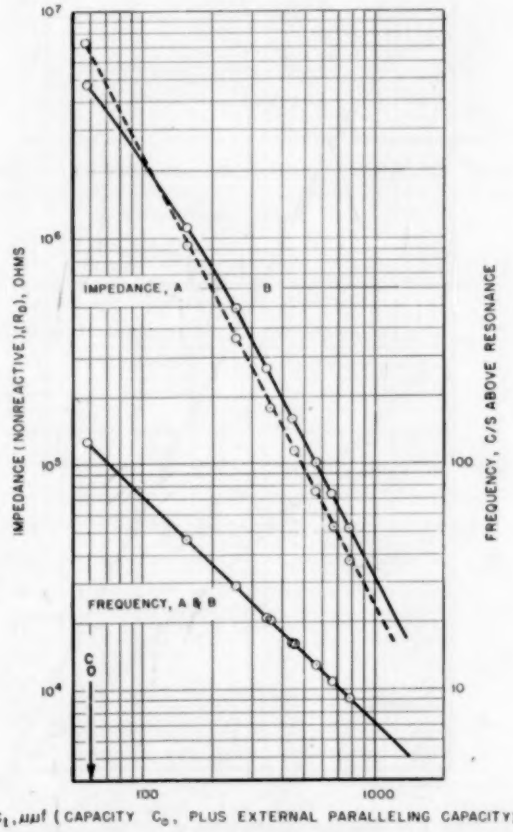


FIGURE 5.—*Electrical characteristics of a 100-kc quartz-crystal unit: GT-cut, metal-film electrodes, wire-mounted crystal, and evacuated container.*

possible operation of the crystal unit at more than one frequency.

R_s could be computed from eq2 for any value of R_p and the corresponding C_t on the straight portion of the curve; however, the value of C_o would have to be measured or supplied by the manufacturer. In short, a set of curves, as shown in figures 6 and 8, supplies all the essential equivalent electrical characteristics of a crystal unit when either f_r or f_a at C_o is also given. L, C, and Q_x of the crystal unit can be determined from eq11, 14, 15, and 16 as C_o, Δf, and R_s are known. On the other hand, a set of crystal-unit data omitting any of these fundamental parameters (i. e., C_o, Δf, R_s, and f_r or f_a) seems to be inadequate in stating the relative merit of a quartz-crystal unit. It is here assumed that data on

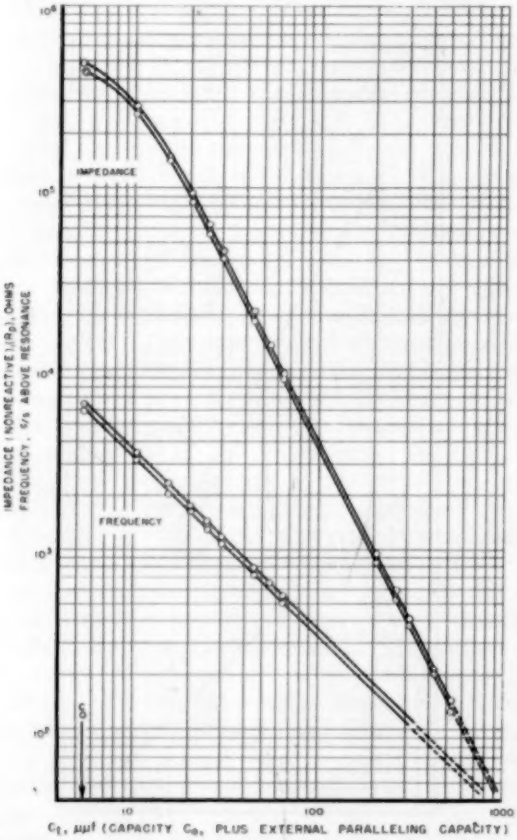


FIGURE 6.—*Electrical characteristics of two type CR–1 crystal units: BT-cut, metal-film electrodes, wire-mounted crystal, plastic container.*

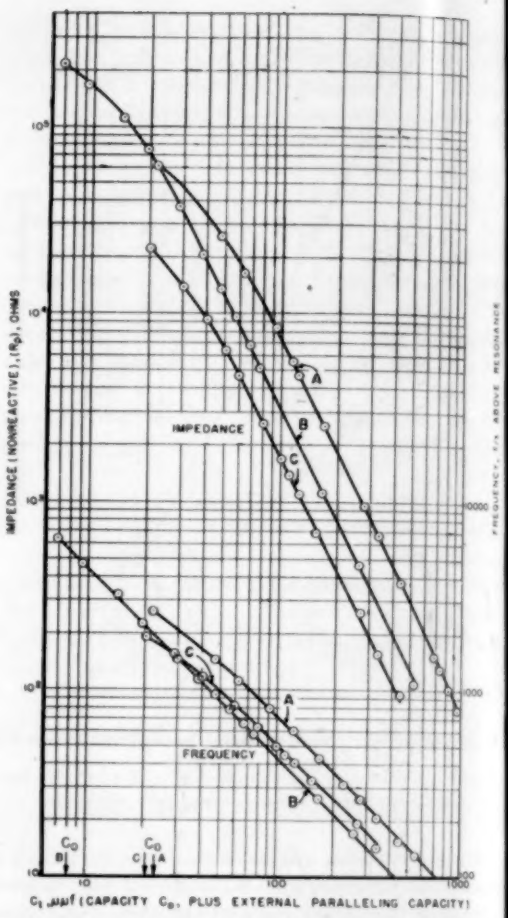


FIGURE 7.—*Electrical characteristics of four "normal" 8.7-Mc crystal units (BT-cut).*

A, Represents two crystals having almost identical impedance and frequency characteristics. Both are air-gap, pressure mounted; one a CR-1, the other an FT-243 type; *B*, FT-243 crystal unit with metal-film electrodes and spring-clip mounting; *C*, FT-243 crystal unit with air-gap electrodes and pressure mounting.

parameter variations with temperature are always indispensable.

Figure 9 shows the main (oscillator-controlling) response (curve *A*) of an unplated 8.7-Mc unit and the response (curve *C*) adjacent to it, the two having an f_a separation of 2,990 cycles. Placing the same crystal in a polystyrene holder extended the straight portion of the R_p curves (*B* and *D*) to values of C_t beyond C_o. These data were taken primarily in an attempt to separate holder losses from losses that might conceivably be coupled

into the first response by the proximity of a second response. It may be seen that up to $C_t = C_o$ the departure of the R_p curve below C_o the sharpness of the peak of the R_p curve as well as the high R_p values of the adjacent response suggest little coupling effect.

Equivalent series resistance and reactance values at frequencies above and below resonance are shown in figure 10 for one of the normal, plated, wire-mounted 8.7-Mc units. The measurements were made with the r-f bridge, which limited the range to the values shown. These curves could be extended to higher positive values of X_e by the use of the Q-meter data and eq1. No attempt was made at this time to measure higher negative values of this parameter.

It was of interest to compare the behavior of the parameters of a secondary and primary response of a normal crystal (with the two responses widely separated). The R_p and frequency versus C_t curves of a large secondary response of one of the wire-mounted units are shown in figure 11. A considerable departure from a 1:1 slope may be observed in the frequency curve, whereas the R_p curve seems to have a normal slope.

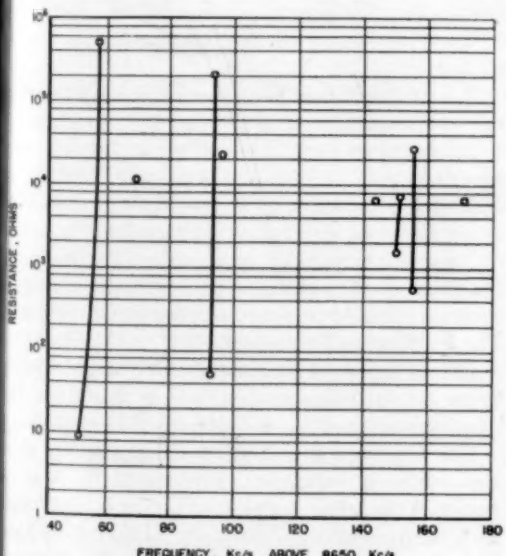


FIGURE 8.—*Frequency-response spectrum of a metal-film electrode, wire-mounted crystal unit of the CR–1 type.*

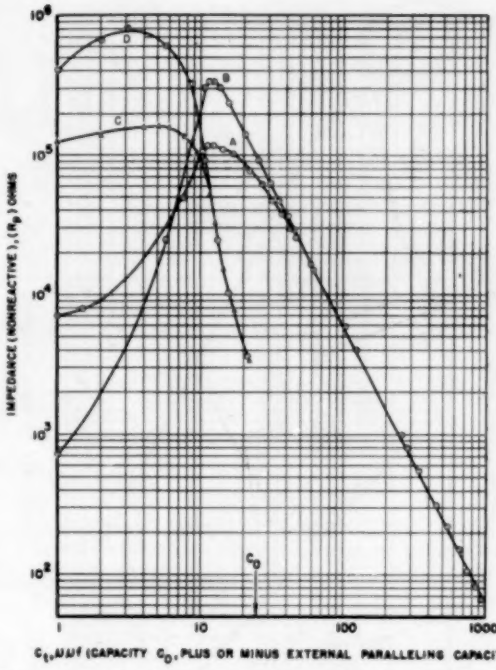


FIGURE 9.—*Impedance measurements above and below antiresonance of the first two adjacent responses of an air-gap, pressure-mounted crystal unit of the FT–243 type: 8.7 Mc, BT-cut.*

A, First response (lowest frequency), plastic container; *B*, first response: special low-loss polystyrene container; *C*, second response: plastic container; *D*, second response: special low-loss polystyrene container.

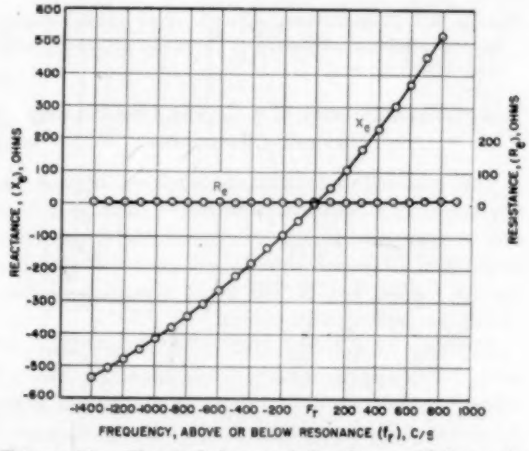


FIGURE 10.— *Electrical characteristics above and below series resonance of a crystal unit of the CR–1 type: BT-cut, 8.7-Mc, metal-film electrodes, wire mounted.*

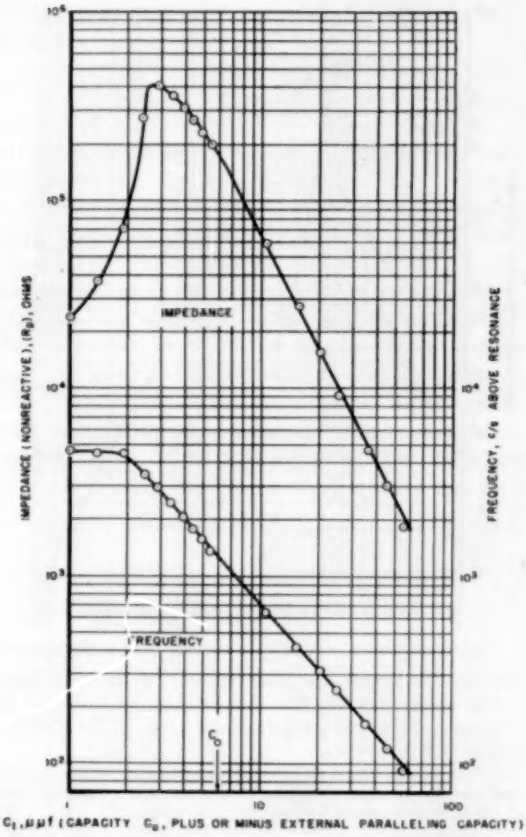


FIGURE 11.— *Electrical characteristics above and below antiresonance of the second large response of crystal unit described in figure 10.*

2. Characteristics of a Crystal Unit Having Interfering Responses

The greatest difficulty encountered in this investigation, as already mentioned, was to locate and to segregate groups of crystal units, the characteristics of which could be measured and the results reproduced at will to an accuracy of that of the measuring equipment.

Stability of activity and of R_s values was observed on approximately 100 unplated, on 25 plated pressure-mounted, and on six plated wire-mounted 8.7-Mc crystal units. Daily measurements were made over a period of weeks. The most stable units were segregated successively by further observations in other equipment. For example, some units were rejected when instability of R_p values was observed in the Q-meter.

It was not intended at the time to study the causes of the instability, which, as may be realized, is a separate problem. Therefore, figure 12 is shown merely to demonstrate the relative instability encountered and the minimum stability required for reliable measurements. It may be noted that all the wire-mounted units were equally stable, whereas approximately 10 percent of the others were stable to the same degree. Some of the units relatively stable with respect to I_g and R_s had R_p and f versus C_t characteristics deviating considerably in slope from the expected 2:1 and 1:1 ratios. This is shown in figure 13. It is seen here that for C_t values between 75 $\mu\mu f$ and C_o, the first response has higher R_p values than the second response. Above 75 $\mu\mu f$ the R_p values of the second response are higher. Thus at a C_t of approximately 75 $\mu\mu f$, this unit operating in an oscillator should jump frequency from one response to the next. This was actually observed in a Miller-type oscillator at the stated C_t value. It should be observed that with this crystal unit the envelopes (or tangents) of the R_p and frequency curves at the two resonances have practically normal slopes. It would, therefore, be misleading to draw an R_p-f-C_t characteristic from a few points. One must be careful not to associate an f_r of one response with the f_a of another.

It is probable that the presence of an interfering response would not show up in test-oscillator circuits now in use. This particular abnormality was detected in other measurements; such as, in improper correlation of I_g versus R_p, operation of an oscillator at a response with a relatively higher R_s, and an unusually wide Δf. The frequency spectrum of the crystal is probably the best indicator of possible presence of interfering responses. The spectrum of this particular unplated unit is shown in figure 14 and should be compared with figure 8. It demonstrates the proximity and the relative values of R_p, R_s, and Δf of all responses.

The low-resistance end of the second response was explored carefully. Equivalent X_e and R_e values of the latter are plotted in figure 15 together with similar curves of normally behaving crystals. Figure 15, a shows R_e and X_e of the first response of this "complex" crystal and 15–B shows these curves for the second response with a minimum R_e at a frequency above f_r. Figure 15, c and d show the same characteristics of the major

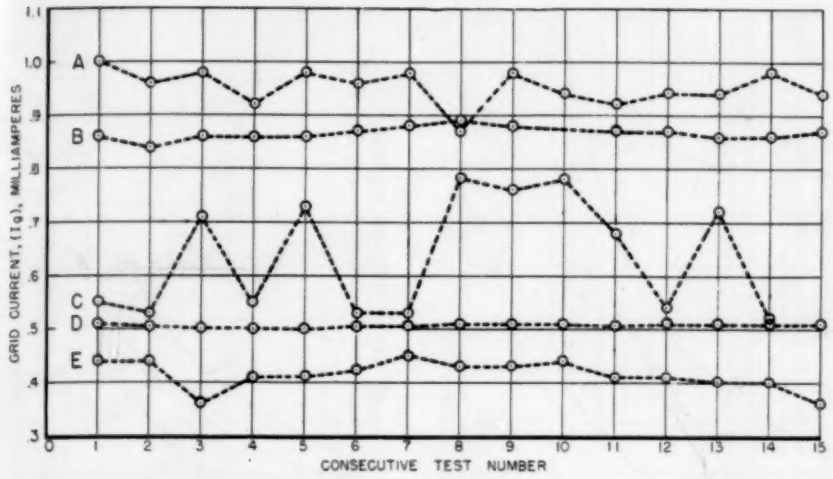
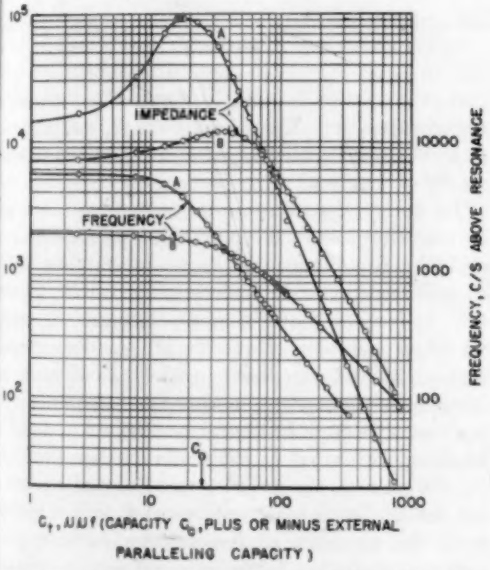


FIGURE 12.—*Crystal unit stability in terms of grid-current variations of a Miller-type oscillator.*

Consecutive tests were made at approximately 24-hour intervals. *A*, an air-gap crystal unit which represented the stability of the majority of this e of unit; *B*, an air-gap crystal unit which represented the minimum stability required for reliable measurements; *C*, an air-gap crystal unit which extremely unstable; *D*, a wire-mounted crystal unit with metal-film electrodes. This unit maintained superior stability; *E*, another wire-mounted stal unit with metal-film electrodes. This unit was more representative of the stability of the majority of this type of unit.



GURE 13.—*Electrical characteristics of two interfering responses of an air-gap, quartz-crystal unit.*

A, f_r=8,697.870 kc/s; *B*, f_r=8,700.395 kc/s.

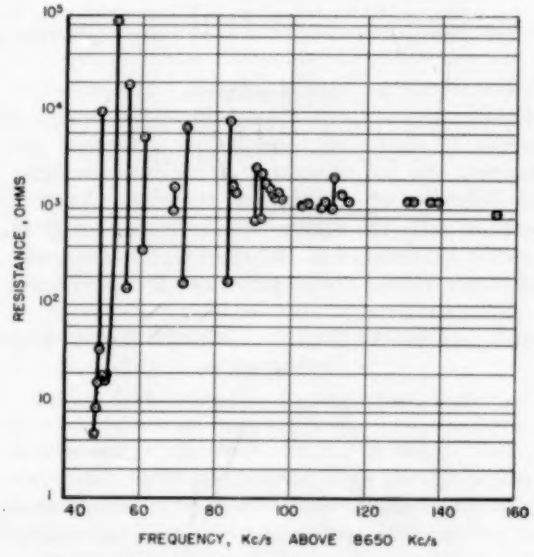


FIGURE 14.—*Frequency response specirum of an air-gap, pressure mounted quartz-crystal unit, typical of those tested.*

The large number of responses of this type of crystal unit may be compared with figure 8, which shows those of a wire-mounted crystal having metal-film electrodes. The position and magnitude of antiresonant impedance of the first two responses are indicative of the behavior shown in figure 13 and described in the text.

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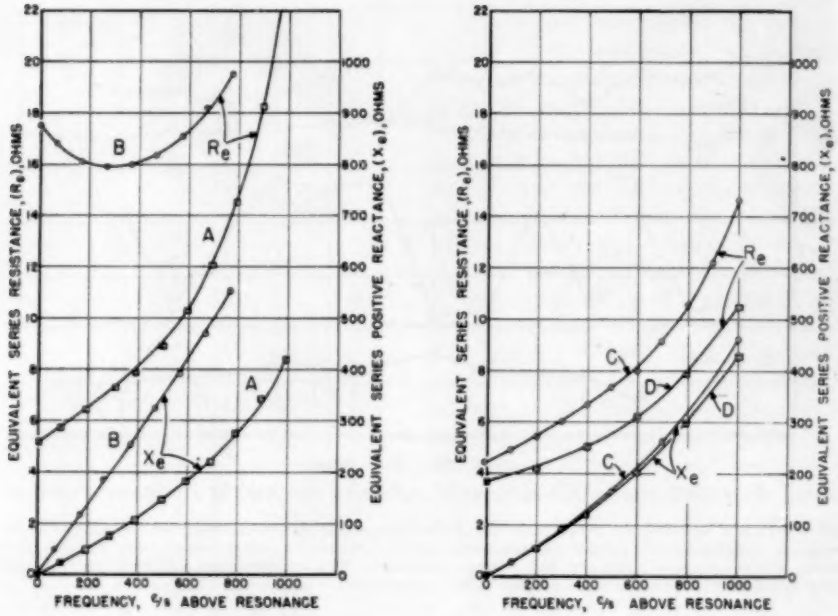


FIGURE 15.—*Electrical characteristics near series resonance of two responses of a complex crystal unit (left), and of the major responses of two "normal" crystal units (right).*

All crystals were 8.7 Mc, BT-cut, air-gap, pressure mounted. *A*, Major response: complex crystal unit; *B*, second response: complex crystal unit; *C*, major response: normal crystal unit; *D*, second response: normal crystal unit. Other characteristics of the complex unit are shown in figures 13 and 14.

responses of two normal crystals. The object in showing these is to demonstrate the practical means of exploring behavior of individual responses, and not necessarily to indicate a manner of behavior of a complex response. As was pointed out, the study of this type of crystal should be handled as a separate problem, employing methods of measurements described here.

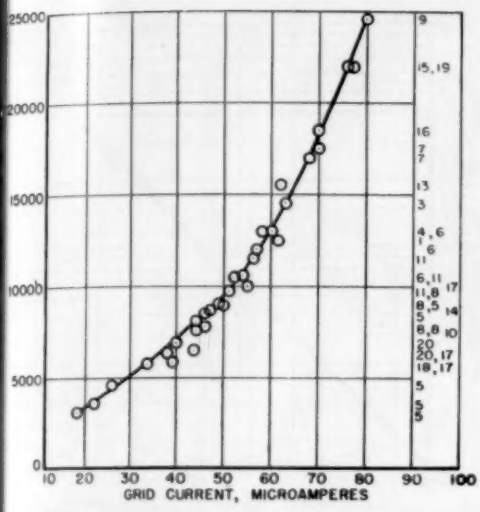
3. Correlation Between Characteristics and Performance

(a) Effect of Amplitude of Vibration and of Temperature

One of the major considerations in the field of quartz-crystal applications for some time has been the establishment of an index of performance to correlate the quality of a unit with its activity and stability in an oscillator, and with its effectiveness in wave-filter circuits.

It has been shown in a number of publications [4, 6, 9] that the activity of an oscillator is a function of the equivalent dynamic resistance R_p of the crystal unit. It was mentioned in the introduction that the higher the Q_x of a crystal unit, the higher its stability and effectiveness in electric circuits. Therefore, both R_p and Q_x seem to be the parameters required to state the relative merits of a crystal unit.

To verify the above relationship, activity and R_p measurements were performed on a number of crystal units of varying degree of stability. The correlation curves are shown in figures 16, 17, and 18. Figure 16 shows the correlation of I_s versus R_p of a number of relatively unstable crystal units. All efforts were made to measure R_p immediately after an activity measurement, to prevent a change in characteristics as a result of handling the crystal unit. To further minimize the differences, the activity was reduced by lowering the oscillator plate voltage. R_p was measured with the Q-meter at low-voltage values. It is seen that there is a fairly good correlation between low and high activity crystals with respective R_p values. Moreover, there is a good correlation between variations in activity of individual crystals and respective variations in their R_p values. For example, crystal 11 had three values of activity obtained at three different times, and three respec-



URE 16.—*Correlation between R_p and I_g of a number of 8.7-Mc crystal units: BT-cut, air-gap type.*

ach crystal unit was measured several times. Numbers 9, 15, etc , are mples of stable crystals. Numbers 5 and 8 are examples of poor stability ll measurements the $R_p - I_g$ correlation is apparent.

e R_p values. All seem to fall well within the rve of the $I_g - R_p$ function for all crystals.

Figure 17 shows this correlation for 13 relatively able units, with three values of ΔC_t and R_p asured at high voltage values (approximately se across the crystal terminals in a Miller-pe oscillator at normal plate voltage). There ms to be good correlation between I_g and R_p all instances.

The correlation between full and reduced tivity and R_p values of five of the most stable its of the group of figure 17 is shown in figure 18. x points were obtained with each unit, three at ll and three at reduced activity. Each of the ree points corresponds to a ΔC_t value of 25, 40, d 70 $\mu\mu f$, respectively, in parallel with C_o. All e R_p values were measured at low voltage values th the Q-meter.

The effect of voltage level across the crystal on characteristics was checked in measuring R_s at ystal-current values from a fraction of a milli-pere up to 100 milliamperes. No differences in is parameter were observed. Low-level versus gh-level R_p curves are given in figure 19 for the re-supported units and in figure 20 for some of e more stable pressure-mounted type. Here ain, the evidence indicates that the amplitude

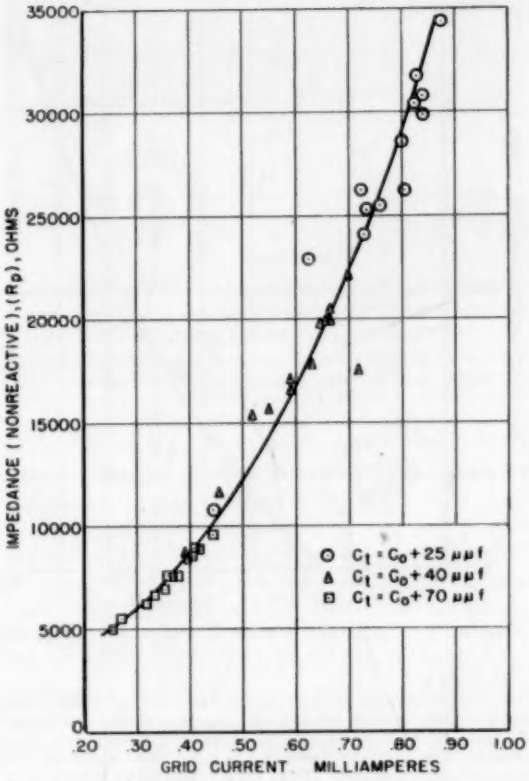


FIGURE 17.—*Correlation between R_p and I_g of thirteen 8.7-Mc, air-gap, pressure-mounted crystal units.*

of the crystal vibration does not affect its fundamental electrical equivalent characteristics. It is believed that the scattering of some of the points in figure 20 were caused by instability of the crystal units and not by an actual difference between the R_p values at the two levels.

Figure 21 shows the temperature effect and correlation between series resistance (R_s) and grid current in a Miller-type oscillator of two wire-mounted crystal units. Although for crystal A both I_g and R_s show some random variations about a fairly constant average value, for crystal B they have definite slopes of opposite sign.

As I_g is a function of R_p it is also a function of R_s and of C_t (see eq 2). Observations were therefore made on the effect of temperature on C_o. No detectable variations were found. It may then be assumed that the I_g variations were caused entirely by R_s changes.

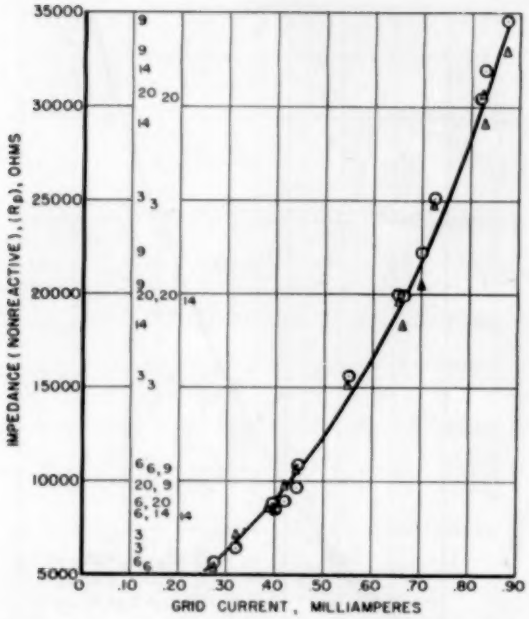


FIGURE 18.—*Correlation between R_p and I_g at two different r-f voltages of five 8.7-Mc crystal units selected for good stability.*

The circles represent measurements at impedance and voltage values corresponding to normal operating conditions in a Miller-type oscillator. The triangles represent values for approximately 10 percent of the above voltages. Three ΔC_2 values were used to obtain three corresponding R_p values for each crystal unit.

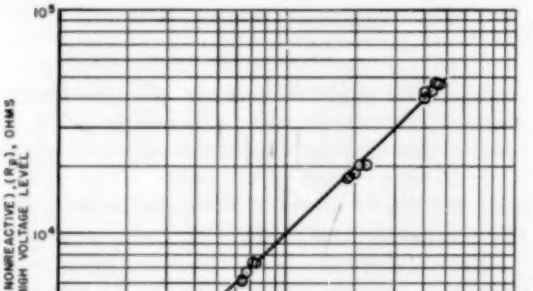


FIGURE 19.—*Correlation between R_p values measured at high and at low r-f voltages across the crystal.*

Five 8.7-Mc crystal units (metal-film electrodes, wire mounted) were measured by using four different values of shunting capacitance (ΔC_2).

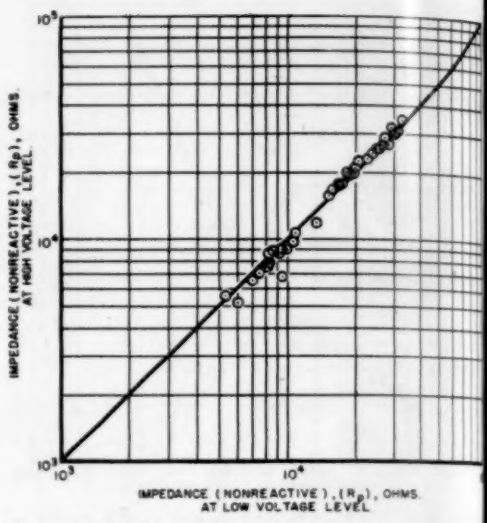


FIGURE 20.—*Correlation between R_p values measured high and at low r-f voltages across the crystal.*

Five 8.7-Mc crystal-units (air-gap, pressure mounted) were measured using four different values of shunting capacitance (ΔC_2).

Variations of R_p were measured with the crys under test placed in a temperature-controll cabinet and connected to the impedance brid through a half-wavelength coaxial cable. Corre tions were made for losses in the cable. difficulties were encountered in the application a coaxial cable to these measurements.

Temperature effects on the relative position crystal-unit responses and on their R_p, R_s, and values were measured as a preliminary step in t study of activity dips. They are shown in figu 22 for a normal wire-mounted crystal unit. Thr

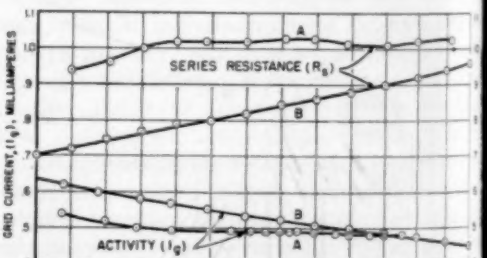
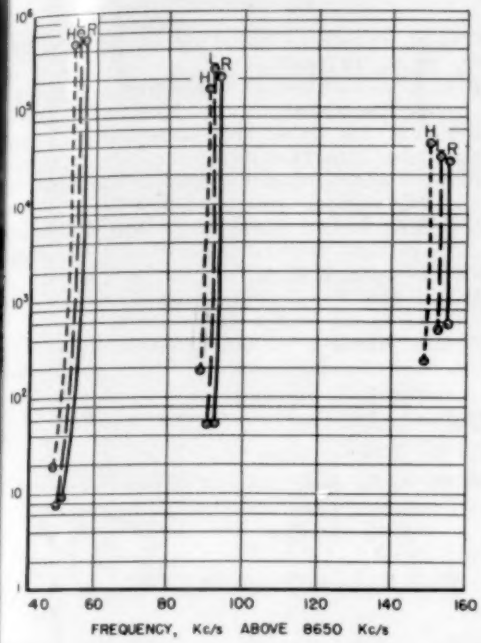


FIGURE 21.—*Variation of the series resistance of cry units and of the grid current with temperature.*

8.7-Mc crystal unit: *BT*-cut; metal-film electrodes, wire mounted. refers to one unit; "*B*" to the other.



URE 22.—*Effect of temperature on three relatively large, nearby responses of an 8.7-Mc crystal unit; BT cut, metal-film electrodes, wire mounted (high, low, and room temperatures).*

rge responses only are shown merely to demonrate the effectivenesss of the method. Other sponses of normal as well as of complex crystal nits were under observation; the results are as t inconclusive and are not given here.

Another graphical presentation of the effect of mperature on the quartz crystal unit is shown figure 23. In curve *A*, a relatively high crystal rrent resulted in a resonance frequency turning oint at an apparent ambient temperature of 3° C. ctually, the high crystal current brought the nclosed crystal plate to a temperature of about 4° C (the "normal" turning point), even though e ambient indicating thermometer read 3° C. urve *B* shows the resultant shift in frequency rning point to an ambient temperature of 15° C the crystal assembly was removed from its nclosure and was thereby exposed to free ventiation. In curve *C*, the crystal current was made

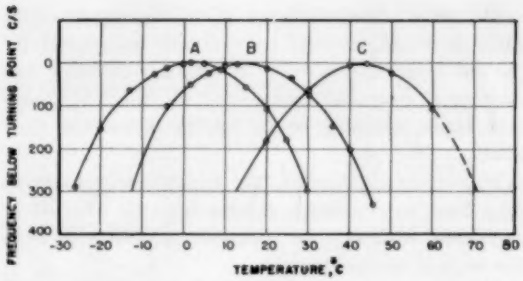


FIGURE 23.—*Effect of operating conditions on temperature and frequency turning position at resonance of an 8.7-Mc crystal; BT cut, metal-film electrodes, wire mounted.*

A, Crystal in plastic container, measured with relatively high crystal current; *B*, same as *A*, with crystal removed from container; *C*, crystal in plastic container, measured at resonance with relatively low crystal current.

negligible and a full 44° C ambient temperature was necessary to bring the crystal plate to its frequency turning-point temperature.

Thus any predetermination of frequency turning point with temperature by a manufacturer or a design engineer must take into consideration at least the approximate amplitude of oscillation expected of the quartz crystal unit. This is in keeping with the observation that the performance index and Δf versus C_t curves used in design work should be accompanied by temperature data for a more complete expression of the characteristics of a quartz-crystal unit.

V. Conclusion

It was shown that comprehensive data on electrical characteristics of quartz-crystal units may be obtained with r-f bridges and *Q*-meters and a source of adjustable stable c-w frequency. Impedance above and below the maximum antiresonance frequency, up to 5,000,000 ohms, may be measured to ± 5 percent or better.

Graphical presentation of measured characteristics as straight lines is a form believed to be particularly suitable for design purposes as they supply essential electrical characteristics.

Results indicated that a good crystal unit was practically unaffected by the normally used voltages across the crystal unit, i. e., no changes with amplitude were observed on units whose series resistance was constant with temperature.

Electrical characteristics of interfering or overlapping responses may be precisely measured by the methods described. Measuring circuits employing the crystal under test as the frequency-controlling element could hardly serve the purpose.

Measurements based on frequency presetting may lead to erroneous results because of shift of responses with crystal currents, affecting in turn the crystal temperature.

The greatest difficulty in measuring electrical characteristics and establishing figures of merit of quartz-crystal units seemed to be the inability to reproduce results as a consequence of changes in the unit. This difficulty could apparently be entirely eliminated by superior types of mounting and construction. The crystal unit would then have good possibilities as reference standards of impedance as well as frequency.

The investigations described were of great value in connection with the precision calibration of new types of crystal unit test sets.

VI. References

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Ionization and Dissociation of *cis*- and *trans*-2-Butene by Electron Impact*

By Vernon H. Dibeler

A study has been made of the appearance potentials and relative abundance of a number of ions from the mass spectra of *cis*- and *trans*-2-butene. The appearance potentials were found to be in generally good agreement with spectroscopic data. The mass spectra of the 2-butenes were compared with those of 1-butene and isobutene. The $C_2H_5^+$ ion was found to be the only ion showing a significant difference between the 2-butene isomers. This difference approached a maximum with ionizing electrons of 40-volt energy and remained constant up to energies of 100 volts.

I. Introduction

The ever increasing interest in the use of the mass spectrometer as an analytical instrument, especially for hydrocarbon analyses, has made it desirable to accumulate complete mass spectra for most of the hydrocarbons encountered in the petroleum and synthetic rubber industries below mass 150 or having a vapor pressure of not less than several millimeters of mercury at room temperature. No less important are the resultant data on energies and unimolecular reactions obtained from the mass spectrometric studies of ionization and dissociation by electron impact of gases at pressures of the order of 10^{-4} millimeter of mercury. Because a comparison of observations of dissociation processes of several related molecules will contribute more information about the properties of the ions produced and the manner in which they are produced than the study of one molecular species, it is the purpose of this paper to extend the data on the lower hydrocarbons to include the *cis* and *trans* isomers of 2-butene. Various authors have already reported data on methane [1],[1] ethylene [2, 3], ethane [4, 5], allene [6], propylene [6, 7], isobutene [7], 1-butene [8], propane [6, 7], *n*-butane [5], and isobutane [5]. In most of these cases it has been possible to determine with the aid of the mass spectrometer what species of ions are produced from a particular molecule by a measure of the mass-to-charge ratio. It is also possible to determine the relative probabilities of formation of each ionic species under given conditions in the ionization chamber. If the energy of the bombarding electrons is controlled and measured, one is able to determine minimum energies necessary to produce any ionic species. In the case of a loss of an electron from the parent molecule, the minimum energy required is known as the ionization potential, I (X^+), of the molecule. The energy at which the ionized parent molecule dissociates into two or more fragments, one of which is an ion, is called the appearance potential, A (X^+), of the ion. The ionization potential is of interest for comparison with data obtained by spectroscopic or theoretical methods. The appearance potentials give information on the heat of dissociation of the molecule though in general they merely set an upper limit to the energies involved. The mass spectrometer data give no information as to the state of aggregation of the uncharged products of dissociation or as to the kinetic energy of the products of ionization. Nevertheless, these data are an important source of additional information on molecular structure and binding energies [9].

*This work was financed in part from funds made available by the Reconstruction Finance Corporation, Office of Rubber Reserve.

[1] Figures in brackets indicate the literature references at the end of this paper.

II. Experimental Procedure

The mass spectrometer used for the present work has been described in several papers [10]. Therefore, only a brief review of the more important details will be presented. The ionization chamber and 180-degree analyser tube were horizontally supported between the pole pieces of an electromagnet. The strength of the magnetic field was such as to deflect ions of a mass-to-charge ratio of 12 along the axis of the analyser tube at an ion-accelerating potential of 2,500 v. A schematic drawing of the ionization chamber and voltage supplies is given in figure 1. The lines of force of the magnetic field are parallel to the electron ribbon. The path of the ion beam is

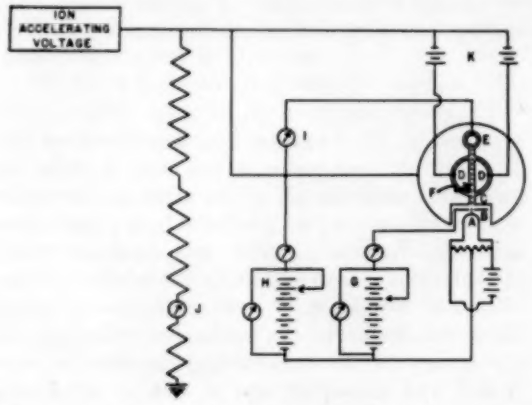


FIGURE 1.—*Schematic drawing of the ionization chamber and power supplies.*

A, Filament; *B*, first electron slit; *C*, second electron slit; *D*, ion pusher; *E*, electron catcher; *F*, electron ribbon; *G*, electron accelerating power supply and meters; *H*, ionizing power supply and meters; *I*, catcher current; *J*, ion accelerating meter; *K*, pusher voltage supply.

downward, perpendicular to the plane of the paper. The energies of the ionizing electrons obtained from a tungsten filament were controlled by a wirewound potentiometer and read on a calibrated University model sensitive research meter, which could be read directly to 0.2 v on the 15-v scale and to 1 v on the 75-v scale. The voltage of the second (ionizing) electron slit was varied, whereas that of the first slit was maintained at 5 v. The filament was mounted in a low-pressure region from which the electrons enter the ionization chamber through a very small slit to minimize interference from products of thermal cracking. Observations on products of primary processes were assured by determining the linear variation of the positive ion current with electron emission and with the pressure of the sample in the ionization chamber.

The *cis*-2-butene and *trans*-2-butene were samples of high purity prepared by J. A. Hinckley, Jr., on the Koppers Fellowship at the Mellon Institute of Industrial Research, Pittsburgh, Pa. The amounts of impurity in these samples were determined by measurements of freezing point by A. R. Glasgow, Jr., under the supervision of Frederick D. Rossini, in the National Bureau of Standards section on Thermochemistry and Hydrocarbons, according to the method described by Glasgow, Streiff, and Rossini [11]. The mole fraction of impurity in *cis*-2-butene is 0.004 ± 0.0010; that in *trans*-2-butene is 0.0181 ± 0.0012. From the manner of preparation and purification of these samples, it is believed that the impurity in each case is substantially all the other isomer. Liquid samples of suitable size were sealed into lengths of 3-ml glass tubing for convenient introduction into the inlet system. The sensitivity, which we may define as the number of divisions of $C_4H_8^+$ ion on the photographic record per micron of sample pressure behind the leak, was such as to give approximately 350 divisions of $C_4H_8^+$ ion for 30 μ of sample pressure for both *cis*- and *trans*-2-butene. All data were automatically recorded by a photographic oscillograph.

The determination of ionization and appearance potentials has been thoroughly discussed by L. G. Smith [1] and Stevenson and Hipple [5, 12]. The procedure used in determining the values reported here was the method of "initial breaks" as described by Stevenson and Hipple [5]. The voltage scale for the hydrocarbon ions was corrected for "contact potential," using the initial break of the ionization efficiency curve of argon. The ionization potential of argon, $I\ (A^+)=15.7$ electron volts (ev) was taken from the tables of Bacher and Goudsmit [13], using the conversion factor 1 ev$=8{,}066$ cm^{-1} to convert from centimeters^{-1} to electron volts. The observed ionization potentials of argon$^+$ and argon^{++} were 13.5 ± 0.1 ev and 41.5 ± 0.1 ev, respectively. The value of $I\ (A^{++})-I\ (A^+)=28.0\pm0.1$ ev is in agreement with values reported for electron impact method [12] and spectroscopic methods [13].

III. Discussion of Results

Figure 2 shows the first portions of the ionization efficiency curves for several of the *cis*- and *trans*-2-butene ions and argon. The curves have been plotted with the ion current scale adjusted to make all slopes nearly equal. Although the appearance potentials were evaluated by extrapolating the smooth curve to intercept the abcissa,

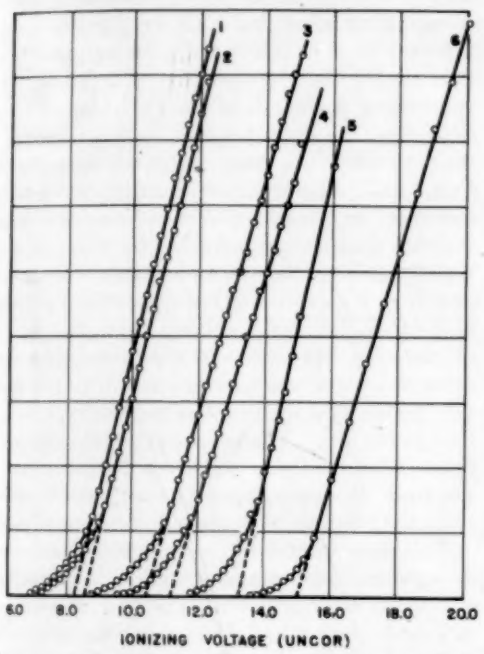


FIGURE 2.—*Initial portions of the ionization efficiency curves for the ions trans*-$C_4H_8^+$ (1), *cis*-$C_4H_8^+$ (2), *trans*-$C_4H_7^+$ (3), *cis*-$C_3H_5^+$ (4), *cis*-$C_2H_2^+$ (5), *and argon*$^+$ (6).

The ordinate is arbitrary and different for some ions.

close checks can be made by comparing the intercepts resulting from extrapolation of the linear portion of the curve to zero ion current.

Table 1 summarizes the appearance potentials of some of the ions in the mass spectra of *cis*- and *trans*-2-butene. Measurements on several ions of 1-butene were made in order to compare experimental details of the present work with that previously reported. Table 2 lists the probable processes by which each ion is formed. Included in table 1 are the values reported for 1-butene and isobutene by Stevenson [8] and Hipple and Stevenson [7] respectively.

TABLE 1.—*Appearance potential of various ions in the mass spectra of cis- and trans-2-butene*

Ion (X^+)	Appearance potential A (X^+) ev				
	cis-2-Butene	*trans*-2-Butene	1-Butene	1-Butene [8]	Isobutene [7]
$C_4H_8^+$	$9.4_1 \pm 0.1$	$9.1_2 \pm 0.1$	$9.6_8 \pm 0.1$	$9.6_8 \pm 0.1$	$8.8_8 \pm 0.1$
$C_4H_7^+$	$11.1_1 \pm 0.1$	$11.2_4 \pm 0.1$	.....	$11.0_7 \pm 0.1$	$11.3_2 \pm 0.1$
$C_3H_5^+$	$11.6_3 \pm 0.1$	$11.7_5 \pm 0.1$	$11.7_8 \pm 0.1$	$11.6_8 \pm 0.1$	$11.5_7 \pm 0.1$
$C_3H_4^+$	12.5 ± 0.2	12.4 ± 0.2	$11.9 \pm 0\ 2$	11.7 ± 0.2	$11.6_2 \pm 0.1$
$C_3H_3^+$	13.8 ± 0.3	14.2 ± 0.3	13.6 ± 0.2	13.8 ± 0.2	14.2 ± 0.5
$C_2H_3^+$	12.2 ± 0.2	12.4 ± 0.2	.....	$11.9_7 \pm 0.1$	15 ± 1
$C_2H_2^+$	10.6 ± 0.2	10.8 ± 0.2	.....	.....	12.1 ± 0.5
$C_2H_3^+$	13.8 ± 0.3	14.0 ± 0.3	.....	13.6 ± 0.3	15.2 ± 0.5

TABLE 2.—*Probable process of ion formation*

Ion	Process
$C_4H_8^+$	$C_4H_8 \rightarrow C_4H_8^+ + e^-$
$C_4H_7^+$	$C_4H_7^+ + H + e^-$
$C_3H_5^+$	$C_3H_5^+ + CH_3 + e^-$
$C_3H_4^+$	$C_3H_4^+ + CH_4 + e^-$
$C_3H_3^+$	$C_3H_3^+ + CH_4 + e^-$
$C_2H_3^+$	$C_2H_3^+ + C_2H_5^+ e^-$
$C_2H_2^+$	$C_2H_2^+ + C_2H_4 + e^-$
$C_2H_3^+$	$C_2H_3^+ + C_2H_3 + e^-$

Except for the first ionization potential, the appearance potentials of the *cis* and *trans* isomers agree within the estimated experimental error. The agreement of the electron-impact ionization potential (9.1 ev) of *trans*-2-butene with the value (9.2 ev) determined spectroscopically by Price and Tutte [14] is gratifying. The small difference in ionization potentials of *cis*- and *trans*-2-butene is in the opposite direction to the difference found by Sugden, Walsh, and Price [15] for *cis*- and *trans*-dichloroethylene, for which the ionization potentials are 9.6_1 ev and 9.9_1 ev, respectively. The ionization potentials of *cis* (9.4 ev) and *trans*-2-butene (9.1 ev) are to be compared with 9.6_5 ev for 1-butene [8], and 8.8_6 ev for isobutene [7].

Both 2-butenes resemble other unsaturated hydrocarbons so far studied by electron impact, with the exception of 1-butene, in that the difference in appearance potentials of the $C_4H_8^+$ ion and the $C_4H_7^+$ ion of both 2-butene isomers is about 2.0 ev. The difference in appearance potentials of the same ions in 1-butene is 1.4 ev [8]. This is very near to the value (1.2 ev) for the difference in appearance potential of the parent ion and the parent ion minus one hydrogen atom of the saturated hydrocarbons. The relative

abundance of the $C_4H_7^+$ ion in the 2-butenes is about the same as that in 1-butene and about 20 percent greater than the abundance of the same ion in isobutene.

Rossini [16] lists the relative stabilities of the butenes as 1-butene (0.00 ev), *cis*-2-butene (0.080 $\pm$0.005 ev), *trans*-2-butene (0.121 $\pm$0.005 ev), isobutene (0.167 $\pm$0.011 ev). The experimental error of the electron-impact values reported for the appearance potentials of the $C_3H_5^+$ ion does not allow stability measurements on the *cis* and *trans* isomers. Comparison with 1-butene and isobutene, however, is practical. From Rossini's list of relative stabilities given above, isobutene is more stable than *cis*-2-butene by approximately 0.09 ev. However, the appearance potentials determined in this work for the $C_3H_5^+$ ion from *cis*-2-butene is 11.6_8 ev, whereas that ion from isobutene is 11.5_1 ev, as determined by Stevenson and Hipple [7]. This indicates that the 2-butene configuration of the $C_3H_5^+$ ion is a total of 0.24 ev less stable than the corresponding isobutene ion. Again from Rossini, *cis*-2-butene is more stable than 1-butene by 0.08 ev. As the appearance potentials of the $C_3H_5^+$ ions from both these molecules agree within experimental error, the 1-butene structure of the $C_3H_5^+$ ion is apparently a total of 0.32 ev less stable than the isobutene configuration. This checks Stevenson's findings [8], and supports his assignment of about 0.4 ev as the lower limit for the activation energy of the reaction

$$CH_2CHCH_2^+ + CH_3 \longrightarrow CH_3CH_2CHCH_2^+$$

(assuming that $CH_2CHCH_2^+ + H \longrightarrow C_3H_6^+$ requires no activation energy) to demonstrate that the allyl ion is at least 0.1 ev more stable than the isoallyl ion. Stevenson has also shown [8] that other electron-impact data and chemical evidence can be reconciled if activation energies for addition of radicals to the vinyl ion are assumed.

The ionization potential of methyl acetylene is 11.25 ev [15], whereas that of allene is 9.9 ev [6]. Although the exact appearance potential of the $C_3H_4^+$ ion is uncertain, the value for the 2-butenes (12.5 ev) being 0.8 ev higher than the same ion for 1-butene would seem to indicate that the $C_3H_4^+$ ion has the methyl acetylene structure rather than the allene structure as reported for the same ion formed from 1-butene [8]. It seems probable then that the CH_3 group and the hydrogen atom forming the unionized products of the process originate from adjacent carbon atoms rather than the same carbon atom.

The appearance potential of the $C_2H_5^+$ ion of the 2-butenes (12.2 ev) combined with the ionization potential of the ethyl radical (8.6_7) reported by Hipple and Stevenson [5, 17], yields a dissociation energy D (C_2H_5-C_2H_3) = 3.5 ev for the reaction 2-butene $\longrightarrow C_2H_5^+ + C_2H_3$, in agreement with that previously reported [8]. The similarity of appearance potentials of the $C_2H_5^+$ ion of *cis* and *trans*-2-butene indicates that both isomers require approximately the same energy to dissociate to a $C_2H_5^+$ ion. At electron energies greater than 20 v, however, the mass spectra of the two isomers indicate that the probabilities for this process are slightly different for the two isomers (see tables 3 and 4). The relatively low appearance potentials of the $C_2H_4^+$ ion (10.6 ev) and the $C_2H_3^+$ ion (13.8 ev) indicate that these ions are formed by a simple dissociation process with one set of products and very probably a single unionized fragment in addition to the ion. The similarity of the appearance potential of the $C_2H_3^+$ ion of the 2-butenes to that ion from 1-butene supports Stevenson's calculation of the ionization potential of the vinyl radical.

The mass spectra of *cis*- and *trans*-2-butene for various ionizing voltages are given in tables 3 and 4. At an ionizing potential of 50 v, the intensity of ion current for the $C_4H_5^+$ ion is given an arbitrary value of 100, in accordance with the practice at this laboratory. The abundances of all other ions are made relative to this value. Some of the less abundant ions of each carbon group have been omitted for the sake of brevity. Also omitted for the same reason are the doubly charged ions with a mass to charge ratio of 25.5, 26.5, and 27.5 originating from the ions $C_4H_5^{++}$, $C_4H_5^{++}$, and $C_4H_7^{++}$, respectively. These first appear at about 40 ev for each isomer. Also omitted are the two metastable ions at 30.0 and 37.0 as reported by Hipple, Fox, and Condon [18] and an additional metastable ion at 15.3, probably originating in the same manner as that one reported for 2-pentene by the same authors. All three metastable ions appear below 20 ev for both isomers.

TABLE 3.—*Mass spectrum of cis-2-butene* [a]

V_I	m/e								
	56 ($C_4H_8^+$)	55 ($C_4H_7^+$)	54 ($C_4H_6^+$)	53 ($C_4H_5^+$)	52 ($C_4H_4^+$)	51 ($C_4H_3^+$))	50 ($C_4H_2^+$)	42 ($C_3H_6^+$)	41 ($C_3H_5^+$)
20	93.6	19.0	2.7	2.3				0.4	102
30	94.6	33.0	6.1	10.3	1.5	2.5	0.7	5.1	155
40	98.0	36.0	7.0	13.2	3.3	8.3	5.9	5.8	172
50	100	38.6	7.3	13.7	3.5	10.4	10.3	6.0	187
60	102	40.1	7.2	12.4	3.4	10.6	11.6	6.1	186
70	105	42.2	7.5	14.2	3.6	10.9	12.5	6.4	190
80	107	43.1	7.7	14.5	3.4	11.0	13.0	6.6	187
90	105	42.8	7.8	14.4	3.2	10.7	14.4	6.5	186
100	107	43.3	7.8	14.0	3.2	10.5	14.5	6.6	188
	40 ($C_3H_4^+$)	39 ($C_3H_3^+$)	29 ($C_2H_5^+$)	28 ($C_2H_4^+$)	27 ($C_2H_3^+$)	26 ($C_2H_2^+$)	15 (CH_3^+)	14 (CH_2^+)	2 (H_2^+)
20	6.0	14.4	11.6	30.6	4.7	0.9	1.0		0.4
30	10.7	49.1	22.5	48.3	37.1	5.8	3.7	0.4	.5
40	12.3	64.9	25.7	55.2	57.0	14.5	7.4	1.1	.5
50	13.2	69.2	26.7	57.7	62.6	20.0	9.9	1.8	.6
60	13.5	70.8	27.2	58.9	64.0	22.8	11.3	2.3	.7
70	14.0	73.3	28.0	60.8	64.9	24.6	11.9	2.7	.8
80	14.2	73.7	28.6	61.9	65.5	25.6	12.3	3.0	.9
90	14.1	72.7	28.3	61.0	63.4	25.3	12.2	2.9	(b)
100	14.1	72.4	28.1	61.6	62.9	25.4	11.9	2.9	(b)

[a] The relative abundances have not been corrected for presence of C^{13} and D.
[b] No measurement made.

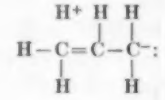
TABLE 4.—*Mass spectrum of trans-2-butene* [a]

V_I	m/e								
	56 ($C_4H_8^+$)	55 ($C_4H_7^+$)	54 ($C_4H_6^+$)	53 ($C_4H_5^+$)	52 ($C_4H_4^+$)	51 ($C_4H_3^+$)	50 ($C_4H_2^+$)	42 ($C_3H_6^+$)	41 ($C_3H_5^+$)
20	80.9	16.7	2.3	2.1				2.8	87.9
30	93.0	32.8	5.7	10.8	1.4	2.5	0.7	5.0	150
40	95.5	36.9	6.4	13.7	3.2	7.9	5.7	5.4	166
50	100	40.0	6.8	14.5	3.6	10.2	10.0	5.9	194
60	104	42.4	7.1	15.2	3.4	10.8	11.7	6.3	191
70	105	42.9	7.1	15.3	3.4	11.0	12.4	6.4	192
80	105	43.5	7.0	15.2	3.4	10.8	12.7	6.3	193
90	103	42.7	6.9	14.9	3.2	10.4	12.6	6.3	191
100	105	43.7	7.0	15.1	3.3	10.5	12.7	6.5	193
	40 ($C_3H_4^+$)	39 ($C_3H_3^+$)	29 ($C_2H_5^+$)	28 ($C_2H_4^+$)	27 ($C_2H_3^+$)	26 ($C_2H_2^+$)	15 (CH_3^+)	14 (CH_2^+)	2 (H_2^+)
20	4.7	14.8	11.5	25.1	3.7	0.5	0.7		0.3
30	9.8	46.3	25.7	46.4	35.3	5.2	3.2	0.4	.5
40	11.3	59.6	30.3	52.7	53.2	12.7	6.6	1.0	.6
50	12.3	65.7	32.3	56.3	59.1	18.1	9.0	1.6	.7
60	13.0	68.8	34.3	59.1	62.7	21.4	10.3	2.2	.7
70	13.2	69.5	34.2	59.4	62.4	22.6	11.0	2.5	.8
80	13.1	69.5	34.3	59.7	62.2	23.6	11.1	2.6	.8
90	13.0	68.2	33.9	58.9	59.9	23.1	11.0	2.7	(b)
100	13.2	69.1	34.5	59.9	60.5	23.3	11.0	2.5	(b)

[a] The relative abundances have not been corrected for presence of C^{13} and D.
[b] No measurement made.

For electron energies of 50 v or more, there appears to be little difference in the *cis* and *trans* mass spectra, especially for ions resulting from the loss of an electron, or a single unit such as a methyl group or hydrogen atom, or the fracture of the double bond splitting the molecule in half. See, for example, the similarity of the sensitivities of the two isomers and the similarity of abundance of the $C_4H_7^+$ ion, the $C_3H_5^+$ ion, and the $C_2H_4^+$ ion in both *cis* and *trans* isomers.

For 50-v electrons, the relative abundance o the $C_2H_5^+$ ion is 27 percent for *cis*-2-butene and 32 percent for *trans*-2-butene compared to 48 percent for 1-butene and 28 percent for isobutene. The abundance of the $C_2H_5^+$ ion in the 2-butenes is interesting because a $C_2H_5^+$ ion is not expected from the structures of *cis*- and *trans*-2-butene. There are two possible explanations for the presence of this ion. The first possibility is the tendency for some molecules of this type to resonate between several possible structures, each structure contributing to the general characteristics of the molecule. For example, to account for dipole moments of 0.35 for propylene, and 0.37 for 1-butene, Hurdis and Smyth [19] point out that three structures can be written for propylene of the type



Although the contribution of such structures is probably small, the fact that one hydrogen bond may have a partially ionic character is of interest as it is already known that the $C_3H_5^+$ ion in propylene is about 30 percent more abundant than the $C_3H_6^+$ ion. Also it might reconcile the anomaly reported by Stevenson in his work on 1-butene, where the difference in appearance potentials of the $C_4H_5^+$ ion and the $C_4H_7^+$ ion is 1.4 ev. This value is near the difference between the $C_4H_{10}^+$ ion and the $C_4H_9^+$ ion (1.2 ev) of the butanes, although the relative abundance of the $C_4H_7^+$ ion in 1-butene is larger than the relative abundance of the $C_4H_7^+$ ion in isobutene, whereas the abundance of the $C_4H_9^+$ ion in isobutane is about five times the abundance of that ion in *n*-butane. Similar structures for the 2-butenes can be shown to be capable theoretically of dissociating to give $C_2H_5^+$ ions.

A second and more usual explanation of h formation of the $C_2H_5^+$ ion is the process common to many of the hydrocarbons studied by electron impact, namely, isomerization that occurs in the very short time between formation of the ion and subsequent dissociation into fragments. Incidentally, as the shape of the recorded peaks resulting from an isomerization process is exactly the same as that resulting from simpler dissociation processes, one would conclude that the isomerization and dissociation is accomplished before the ion is accelerated by the electrostatic field. Knowing the dimensions of the ionization chamber, it is possible to calculate an upper limit for the time required for a 2-butene ion to isomerize and dissociate to give a stable $C_2H_5^+$ ion. Assuming that an ion of mass M, and charge e, in coulombs, is accelerated from rest in an electric field of E volts, the velocity (cm/sec) after falling through the total potential E, is given by

$$V=\sqrt{\frac{2eE10^7}{M}}.$$

Assuming a pusher potential of 4 v and a distance of 3 mm between the electron ribbon and the ion accelerating slit, the maximum time allowable for isomerization and dissociation to form a stable $C_2H_5^+$ ion is of the order of 10^{-6} second.

Both 2-butene patterns are generally lower than those of 1-butene and isobutene except in the C_2 group, where the abundances of the ions are about half way between 1-butene and isobutene, the former having the highest values. In the C_4 group, all 2-butene ions with the exception of the $C_4H_7^+$ ion, are more abundant than the same ions from either 1-butene or isobutene. The 2-butene $C_4H_7^+$ ion is slightly less abundant than 1-butene and 20 percent more abundant than isobutene.

Figure 3 is a plot of some of the data in tables 3 and 4. All the curves are for ions originating from *cis*-2-butene, with the exception of the $C_2H_5^+$ ion, data for which are given for both *cis* and *trans* isomers. The flat portion of each curve occurs above 50 v, indicating rather stable con-

ditions for recording relative abundances above that voltage. The $C_2H_5^+$ ion is the only ion with significant differences in abundance between *cis*- and *trans*-2-butene. It is obvious from figure 3 that even this difference is small and very constant with increasing ionizing voltage.

It was hoped that the variation of mass spectra of the 2-butenes with energy of the ionizing electrons would be such as to make possible the selection of an ionizing voltage which would allow a more accurate separation of the *cis*- and *trans*-2-butenes in a mixture of the other butenes. Unfortunately, the relatively low abundance of the $C_2H_5^+$ ion, which is the only ion exhibiting a significant difference in abundance between the two isomers, reduces its effectiveness as a means of

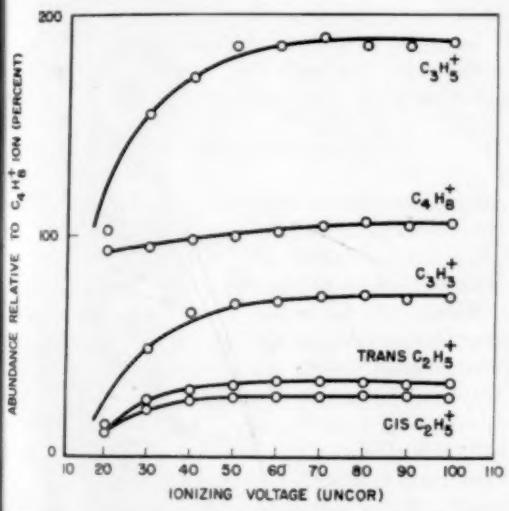


FIGURE 3.—*Upper portion of the ionization efficiency curves for the ions cis-$C_3H_5^+$, cis-$C_4H_8^+$, cis-$C_3H_3^+$, cis-$C_2H_5^+$, and trans-$C_2H_5^+$.*

The abundance of each ion is relative to the abundance of the *cis*-$C_4H_8^+$ ion at electron energies of 50 v.

accomplishing the separation with any reasonable degree of accuracy. Under standard operating conditions the energy of the electron beam is 50 v. There is no evidence to indicate that an advantage can be gained by operating at some other value.

IV. Summary

The appearance potentials and relative abundances of a large portion of the mass spectra of *cis*- and *trans*-2-butene are reported. The ionization potentials of *cis*-2-butene and *trans*-2-butene were found to be $9.4_1 \pm 0.1$ and $9.1_3 \pm 0.1$ ev, respectively. The latter is in agreement with previously determined spectroscopic data. The values for the heat of dissociation of the $C_2H_5-C_2H_3$ bond and the ionization potential of the vinyl radical calculated from *cis*- and *trans*-2-butene are found to be in agreement with those values reported by Stevenson. The mass spectra of *cis*- and *trans*-2-butene are compared with each other and with 1-butene and isobutene. There is no evidence to indicate an advantage in using ionizing energy other than the normal operating value of 50 v when analysing mixtures containing *cis*- and *trans*-2-butene.

The author expresses his appreciation for the many helpful suggestions made throughout the course of this work by Fred L. Mohler of this laboratory. Thanks are also expressed to Harold W. Washburn, of the Consolidated Engineering Corporation, for several suggestions concerning electric circuits made in a private communication.

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Properties of Barium-Strontium Titanate Dielectrics

By Elmer N. Bunting, George R. Shelton, and Ansel S. Creamer

The results on barium-strontium titanates are given for heat treatments, absorption, shrinkage, thermal expansion, dielectric constant (K) at $-60°$ to 85° C, and also for Q, the reciprocal of the power factor, at 25° C for frequencies of 50 to 20,000 *kc/s*. A few measurements of K and Q were made at 3,000 *mc/s*. Specimens matured (absorption less than 0.1 percent) at 1,250° to 1,430° C. K values ranged from 34, for $BaO:4TiO_2$, to several thousand for specimens with compositions on the $BaTiO_3$-$SrTiO_3$ join. Specimens having the composition $BaO:5TiO_2$ were unique in that their temperature coefficient of K was practically zero. Q values ranged from 50 to 100 for test pieces containing over 40 percent of BaO, and from 400 to 10,000 for those with less than 40 percent of BaO. K values did not change appreciably with frequency. Linear thermal expansions between 25° and 700° C ranged from 0.6 to 0.84 percent. Many of these specimens could be used in radio equipment.

I. Introduction

The properties of titanates containing barium and strontium have been investigated only recently [1, 2, 3],[1] although dielectrics containing titanium have been used in radio equipment since 1925 [4], and the high values of the dielectric constant of some of the oxides of titanium have been known since 1903 [5]. Many patents have been issued covering the preparation of dielectrics from titania in combination with such oxides as MgO, ThO_2, ZrO_2, SiO_2 and as titania-filled organic plastics. Some of the titanates were conspicuous because they exhibited outstandingly high values of the dielectric constant [1]. Although many data have been published [1, 2, 3] on specific titanates, a knowledge is desirable of the properties of such materials over a wide range of compositions. In 1944 a systematic study of ceramic dielectrics, of which this paper constitutes the first report, was undertaken at the request of the Army Signal Corps.

II. Preparation of Specimens

A stock of titania, designated TMO, together with chemically pure quality barium and strontium carbonates, were used in the preparation of all specimens with compositions shown in figure 1. Three other grades of titania were tested also.

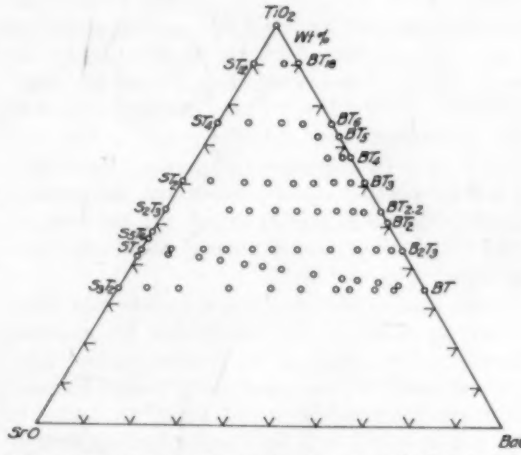

FIGURE 1.—*Ternary diagram for the system* BaO-SrO-TiO_2, *showing compositions studied.*

B=BaO; S=SrO; T=TiO_2.

The chemical analysis, furnished by the maker, and some properties of each of the four grades are given in table 1.

[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1.—*Composition, specific surface, and crystal form of four brands of commercial titanium dioxide, and also the heat treatments and properties of specimens prepared from these materials*

Grade designation	Composition [a]			Specific surface [b]	Crystal form [c]	Heat treatments for 1 hr at—		Shrinkage [d]	Absorption [d]	Dielectric constant (K) at 25° C and 1,000 kc/s	Reciprocal (Q) of power factor at 25° C and 1,000 kc/s
	TiO_2	SiO_2	Al_2O_3								
	Wt %	*Wt %*	*Wt %*	*cm²/g*		*°C*	*°C*	*Percent*	*Percent*		
TMO	98.7	0.25	0.2	39,000	Rutile	1,100	1,305	14.1	3.33	76	182
						1,100	1,350	16.6	0.72	87	1,000
						1,100	1,400	17.6	.02	91	5,200
WD	98.7	.4	.03	36,000	do	1,100	1,305	7.5	10.50	42	7
						1,100	1,350	9.5	9.62	49	6
						1,100	1,425	.....	7.02	(e)	(e)
R	98.2	.5	.1	27,000	do	1,100	1,305	18.3	0.00	97	7,000
						1,100	1,350	19.6	.01	98	7,700
						1,100	1,400	18.9	.01	98	8,800
A	98.8	.2	[f].2	8,000	Anatase	1,400	None	15.8	.00	97	4,700

[a] Compositions furnished by maker.
[b] Determined by R. L. Blaine with the Lea-Nurse apparatus, air-permeability method.
[c] Determined by X-ray diffraction by H. F. McMurdie.
[d] Values obtained after final heat treatment.
[e] Conductance too high for measurement.
[f] Also contains 0.45% alkali.

Weighed batch constituents were added to distilled water containing a wetting agent (2 drops of aerosol per 250 ml of water), and the suspension stirred for 1 hr with a high-speed stirrer. After drying the caked mixture it was passed through a No. 50 sieve and moistened with 10 percent, by weight, of a 2 1/2-percent starch suspension. The moist powder was then dry-pressed at 10,000 lb/in.² into cylinders (5/8 in. in diameter by 3/4 in. long), which, after drying, were heated at 1,100° to 1,245° C for 1 hr. These calcined cylinders were pulverized and passed through a No. 325 sieve. After moistening with 5 percent, by weight, of a 2 1/2-percent starch suspension, the powder was dry-pressed at 20,000 lb/in.² into the form of disks 1/8 in. thick and of various diameters ranging from 1/4 in. to 1 in.

In all heat treatments, the cylinders and disks rested on platinum foil supported by alumina plaques. After heating the specimens overnight to about 1,000° C in an electrically heated furnace, the maturing temperature of 1,250° to 1,430° C was attained in 3 to 5 hr, using a heating rate of about 3 deg C a min, and was held for either 1 or 2 hr within ±5 deg C of the desired temperature. The furnace heating chamber was heated on all sides and was uniform in temperature within ±5 deg C. All temperatures were measured with calibrated Pt to Pt-Rh thermocouples.

III. Test Methods

Absorption was determined by immersing the weighed specimen in chemically pure carbon tetrachloride, where it remained while the liquid was boiled for 5 hr and allowed to cool. After quickly drying the surface of the specimen, it was weighed in a stoppered bottle. Carbon tetrachloride was used instead of water to avoid any hydration of the specimens. Any gain in weight was divided by the density of the CCl_4 in order to find the equivalent gain, had water been used. Percentage absorption equals equivalent gain in weight, divided by dry weight, multiplied by 100. The percentage of shrinkage was obtained from the diameter of the mold used, minus the average diameter of the matured specimen, divided by the diameter of the mold, multiplied by 100.

The dielectric constant (K), and the Q-value[1] were obtained from measurements on a Boonton "Q" meter, type 160–A, whose condenser had been calibrated against a calibrated precision condenser. This meter was operated in a cabinet controlled at 25° ± 0.5° C and a relative humidity of 40 percent or less. The titanate specimens were heavily coated on both sides with a silver

[1] This value constitutes a "figure of merit" in radio-circuit design, and when greater than 10, is nearly equal to the reciprocal of the cosine of the phase angle (θ). High Q-values for inductors and condensers are necessary for good selectivity in tuned circuits.

paste and heated to 750° C in an electric muffle furnace to give silver electrodes about 0.01 in. thick. Any extraneous silver on the side of a disk was removed with fine sandpaper. Specimens were kept at a relative humidity of 40 percent or less and at room temperature for several hours and then at 25° ± 0.5° C for ½ hr before the measurements were made. Disks with a capacity greater than the capacity used in the variable condenser in the instrument were measured in series with a suitable condenser.

The capacitance from which the dielectric constant was computed was determined at 1,000 kc/s, and temperatures ranging from −60° to +85° C, by the resonant circuit[3] capacity substitution method. The specimens were held between brass electrodes in an insulated chamber 1 ft³ in volume. This chamber could be cooled with dry ice or heated by a heating coil, and was controlled to ±0.25° C. Measurements were made at +40°, +60°, +80°, +85°, +70°, +50°, +30°, +20°, +0°, −20°, −40°, −60°, −50°, −30°, −10°, and +10° C. Prior to each measurement, the temperature of the specimen was maintained constant for 15 or more minutes.

Measurements at a frequency of 3,000 mc/s were made on specially shaped specimens in the Massachusetts Institute of Technology coaxial wave guide instrument [6].

Thermal-expansion determinations were made by the interferometer method at a heating rate of ½ to 3 deg C a minute.

IV. Results and Discussion

One of the difficulties encountered in the preparation of titanate dielectrics is the lack of uniformity in commercial grades of titanium dioxide. The four grades investigated varied not only in composition but also in grain size and crystal structure. Consequently, matured specimens of impure TiO_2 did not exhibit identical properties, as illustrated by the data in table 1. Such results, showing grade *WD* to be the least satisfactory for preparing dielectrics of this type, may not warrant the rejection of a given grade for the preparation of dielectrics that contain other materials, such as BaO or SrO. In the experiments on three grades (table 2), the choice of grade was immaterial so far as the properties of matured specimens of $SrTiO_3$ was concerned. The maturing temperature and other properties of specimens may vary considerably for some specimens when different grades of TiO_2 are used.

In table 3 data are given on the composition, heat treatment; absorption; shrinkage; dielectric constant (K); and Q, the reciprocal of the power factor, for matured specimens of the titanates studied.

TABLE 2.—*Properties of barium and strontium titanate specimens prepared from three grades of commercial titanium dioxide*

Grade of TiO_2	Heat treatments [a]		Shrinkage	Absorption	Dielectric constant (K) at 25° C and 1,000 kc/s	Reciprocal (Q) of power factor at 25° C and 1,000 kc/s
	Temperature	Time				
Specimens of $BaO:TiO_2$						
	° C	hr	*Percent*	*Percent*		
TMO	1,385	2	10.6	0.05	1,500	100
WD	1,400	1	10.9	.03	1,650	74
R	1,400	1	6.9	1.07	1,300	144
Specimens of $SrO:TiO_2$						
TMO	1,375	2	15.2	0.01	264	8,000
WD	1,400	1	14.8	.01	270	7,600
R	1,400	1	16.3	.01	270	8,000
Specimens of 57.4% $SrO:TiO_2$+42.6% of $BaO:TiO_2$						
TMO	1,420	2	13.7	0.00	680	10,000
WD	1,430	1	10.7	2.44	655	31
R	1,430	1	9.7	2.22	605	4,800

[a] All preparations were given a preliminary calcination at 1,245° C for 1 hr.

[3] A Hartley oscillator containing a No. 71A tube was used. This was powered on the filament and plate by storage batteries. Resonance was determined on a loosely coupled pick-up circuit, tuned by a precision condenser, and current was indicated by a vacuum thermocouple, using a galvanometer, lamp, and scale.

TABLE 3.—*Composition, heat treatment, absorption, shrinkage, dielectric constant, K, and Q, of bodies in the system* BaO-SrO-TiO_2

Specimen designation	Proportion of end members of join	Composition weight			Heat treatment			Absorption	Shrinkage	Dielectric constant, K, at 25° C and—			Reciprocal, Q, of power factor at 25° C and—		
					No. 1	No. 2									
		BaO	SrO	TiO_2	1 hr at—	Temperature	Time			50 kc/s	1,000 kc/s	20,000 kc/s	50 kc/s	1,000 kc/s	20,000 kc/s
						$SrO:12TiO_2$ $BaO:18TiO_2$									
	Weight percent	*Weight percent*	*Percent*	*Percent*	*Percent*	*° C*	*° C*	*hr*	*Percent*	*Percent*						
ST12	100	0	.....	9.8	90.2	1,100	1,310	1	0.00	16.2	113	113	114	2,500	3,300	2,6
18BS6	36	64	6.2	3.5	90.3	1,100	1,275	1	.00	16.6	83	82	82	1,200	5,400	6,7
BT18	0	100	9.6	.....	90.4	1,100	1,275	1	.00	15.0	75	74	74	260	1,000	7,6
						$SrO:4TiO_2$ $BaO:6TiO_2$									
ST4	100	0	.....	24.5	75.5	1,100	1,350	1	0.00	18.0	148	147	152	800	4,000	1,8
6BS2	75	25	6.2	18.3	75.5	1,100	1,310	1	.01	17.9	120	119	121	5,400	4,000	1,6
6BS5	45	55	13.2	11.3	75.5	1,100	1,275	1	.00	17.9	78	77	76	3,400	3,400	3,5
6BS7	25	75	18.1	6.3	75.6	1,100	1,275	1	.06	16.3	53	53	51	>500	1,550	3,7
BT6	0	100	24.3	.....	75.7	1,100	1,275	1	.01	14.0	46	45	44	85	400	2,2
						$SrO:3.4TiO_2$ $BaO:5TiO_2$									
5BS8	18	82	22.7	5.0	72.3	1,100	1,285	1	0.06	16.2	44	43	42	265	1,600	4,0
BT5	0	100	27.7	.....	72.3	1,100	1,325	1	.04	12.0	39	37	37	1,500	2,300	1,3
						$SrO:2.7TiO_2$ $BaO:4TiO_2$									
4BS8	15	85	27.4	5.0	67.6	1,100	1,300	1	0.01	16.4	43	43	42	>2,000	10,000	5,0
4BS9	8	92	30.4	2.0	67.6	1,100	1,300	1	.01	15.4	37	37	36	>1,600	2,400	4,0
BT4	0	100	32.4	.....	67.6	1,100	1,330	1	.03	16.9	34	34	35	>1,600	2,000	1,7
						$SrO:2TiO_2$ $BaO:3TiO_2$									
ST2	100.0	0.0	.....	39.3	60.7	1,100	1,330	1	0.09	16.3	186	185	185	1,600	4,500	2,0
BS1	84.0	16.0	6.2	33.1	60.7	1,100	1,300	1	.00	19.1	163	162	161	1,700	2,200	1,0
BS3	66.0	34.0	13.2	26.0	60.8	1,100	1,315	1	.00	19.9	121	120	119	5,100	2,100	1,2
BS4	51.5	48.5	18.1	21.1	60.8	1,100	1,315	1	.00	19.2	90	90	90	3,900	2,500	1,6
BS6	39.2	60.8	23.7	15.4	60.9	1,100	1,290	1	.00	19.0	75	75	74	3,300	1,600	1,6
BS7	28.2	71.8	28.0	11.1	60.9	1,100	1,260	1	.01	18.1	64	64	63	2,900	2,100	2,6
BS8	15.9	84.1	32.8	6.3	60.9	1,100	1,260	1	.00	17.4	51	50	49	2,300	1,200	2,6
BS9	8.0	92.0	36.2	2.8	61.0	1,100	1,260	1	.00	17.5	49	49	48	>2,000	1,200	2,6
BT3	0.0	100.0	39.0	.....	61.0	1,100	1,260	1	.03	17.4	44	44	43	720	650	8
						$2SrO:3TiO_2$ $BaO:2.2TiO_2$									
S2T3	100.0	0.0	.....	46.3	53.7	1,100	1,310	1	0.02	16.2	200	200	196	450	2,000	3,3
BS22	71.5	28.5	13.2	33.1	53.7	1,100	1,350	1	.02	17.9	153	151	149	270	650	1,3
BS23	61.0	39.0	18.1	28.2	53.7	1,100	1,360	1	.09	17.1	153	150	149	560	680	1,6
BS25	49.0	51.0	23.7	22.6	53.7	1,100	1,310	1	.02	17.3	148	147	145	1,700	1,500	1,6
BS26	39.5	60.5	28.0	18.3	53.7	1,100	1,290	1	.06	17.6	134	133	138	600	550	7
BS271	29.0	71.0	32.8	13.5	53.7	1,150	1,295	1	.00	17.6	154	153	153	1,200	850	9
BS279	20.7	79.3	36.7	9.6	53.7	1,150	1,295	1	.00	17.5	210	205	200	500	480	2
BS28	12.5	87.5	40.5	5.8	53.7	1,150	1,295	1	.00	16.9	255	255	255	385	170	9
BS29	6.0	94.0	43.5	2.8	53.7	1,150	1,295	1	.00	15.4	215	215	210	130	100	5
BT2.2	0.0	100.0	46.3	.....	53.7	1,150	1,250	1	.00	12.9	97	95	92	140	75	6

TABLE 3.—*Composition, heat treatment, absorption, shrinkage, dielectric constant, K, and Q, of bodies in the system* BaO-SrO-TiO_2—Continued

Specimen designation	Proportion of end members of join		Composition weight			Heat treatment			Absorption	Shrinkage	Dielectric constant, K, at 25° C and—			Reciprocal, Q, of power-factor at 25° C and—		
						No. 1	No. 2									
			BaO	SrO	TiO_2	1 hr at—	Temperature	Time			50 kc/s	1,000 kc/s	20,000 kc/s	50 kc/s	1,000 kc/s	20,000 kc/s
$BaO:2TiO_2$																
	Weight percent	*Weight percent*	*Percent*	*Percent*	*Percent*	*° C*	*° C*	*hr*	*Percent*	*Percent*						
BT2	.....	100	49.0	.....	51.0	1,100	1,290	1	.02	16.4	204	200	197	100	70	35
$SrO:TiO_2$ $2BaO:3TiO_2$																
ST	100.0	0.0	.....	56.4	43.6	1,200	1,375	2	0.01	15.2	260	260	260	5,500	8,000	10,000
B2S1	89.0	11.0	6.2	50.2	43.6	1,100	1,350	1	.01	16.2	260	255	246	370	1,300	7,000
B2S2	76.4	23.6	13.2	43.2	43.6	1,100	1,350	1	.09	16.2	290	285	280	500	850	2,400
B2S3	67.7	32.3	18.1	38.3	43.6	1,100	1,310	1	.07	17.6	315	310	300	2,100	1,900	2,400
B2S4	57.7	42.3	23.7	32.7	43.6	1,100	1,310	1	.06	17.9	380	375	385	1,300	1,000	900
B2S5	50.0	50.0	28.1	28.2	43.7	1,100	1,290	1	.02	17.1	460	450	465	1,000	800	500
B2S6	40.0	60.0	33.7	22.6	43.7	1,100	1,290	1	.03	18.0	670	660	645	650	520	325
B2S72	27.8	72.2	40.5	15.7	43.8	1,100	1,290	1	.03	17.8	970	950	950	210	190	95
B2S83	17.0	83.0	46.6	9.6	43.9	1,100	1,290	1	.04	17.5	1,090	1,070	1,070	110	100	45
B2S9	10.0	90.0	50.5	5.6	43.9	1,200	1,285	2	.02	15.1	910	895	885	80	80	35
B2S95	5.0	95.0	53.3	2.8	43.9	1,200	1,285	2	.00	14.7	845	850	850	80	60	30
B2T3	0.0	100.0	56.1	.....	43.9	1,250	1,300	1	.01	10.8	910	900	890	70	50	25
$SrO:TiO_2$ $BaO:TiO_2$																
B9	90.2	9.8	6.2	50.8	43.0	1,245	1,385	2	0.03	14.3	300	300	295	5,000	4,700	10,000
B79	79.9	20.1	13.2	44.5	42.3	1,245	1,400	1	.03	15.0	355	355	345	>2,300	10,000	10,000
B72	72.5	27.5	18.1	40.0	41.9	1,245	1,400	1	.03	14.6	415	415	405	>2,700	8,000	10,000
B64	64.0	36.0	23.7	35.0	41.3	1,245	1,400	1	.10	13.3	510	515	505	3,000	7,200	10,000
B57	57.4	42.6	28.0	32.4	39.6	1,245	1,420	2	.00	13.7	660	680	670	>5,000	10,000	9,000
B50	50.0	50.0	32.8	28.2	39.0	1,245	1,420	2	.01	14.3	870	900	900	5,700	8,500	1,700
B39	39.0	61.0	40.1	22.0	37.9	1,245	1,420	2	.00	13.2	1,600	1,600	1,600	2,000	4,500	1,200
B34	34.8	65.2	42.8	19.6	37.6	1,245	1,400	1	.02	12.5	2,600	2,600	2,600	1,100	1,700	1,800
B32	32.4	67.6	44.4	18.3	37.3	1,245	1,400	1	.01	12.5	3,300	3,300	3,300	700	1,000	900
B29	29.0	71.0	46.7	16.3	37.0	1,245	1,420	2	.00	12.8	6,000	6,000	6,000	250	550	200
B26	26.8	73.2	48.1	15.1	36.8	1,245	1,400	1	.00	12.3	7,000	7,000	7,000	110	380	165
B23	23.8	76.2	50.1	13.4	36.5	1,245	1,420	2	.00	12.4	7,500	7,500	7,500	30	110	50
B21	21.4	78.5	51.7	12.0	36.3	1,245	1,400	1	.00	11.7	3,300	3,300	3,300	27	110	45
B18	18.5	81.5	53.5	10.4	36.1	1,245	1,400	1	.01	11.5	2,300	2,300	2,300	30	105	45
B16	16.2	83.8	55.1	9.1	35.8	1,245	1,420	2	.00	11.4	1,900	1,900	1,900	35	120	60
B1	10.0	90.0	59.1	5.6	35.3	1,245	1,385	2	.08	13.0	1,500	1,500	1,500	40	110	60
BT	0.0	100.0	65.7	.....	34.3	1,245	1,385	2	.05	10.6	1,500	1,500	1,500	80	100	50
$3SrO:2TiO_2$ $BaO:TiO_2$																
B3S6	40.0	60.0	39.4	26.4	34.2	1,245	1,425	2	0.02	13.2	300	300	300	15	50	165
B3S7	29.0	71.0	46.6	19.2	34.2	1,245	1,425	2	.06	14.6	900	900	900	400	850	700
B3S75	24.7	75.3	49.5	16.3	34.2	1,245	1,425	2	.02	15.9	1,600	1,600	1,600	350	700	400
B3S8	16.3	83.7	55.0	10.7	34.3	1,245	1,430	2	.01	13.5	4,400	4,400	4,400	35	155	80
B3S9	10.0	90.0	59.1	6.6	34.3	1,245	1,425	2	.00	15.6	2,400	2,400	2,400	50	150	75
S_4T_6	.....	.....	.....	52.0	48.0	1,200	1,400	1	0.02	17.5	238	237	238	2,100	5,000	2,900
ST_2	.....	.....	.....	54.0	46.0	1,200	1,400	1	.00	18.2	257	256	256	4,400	3,900	2,900
ST_3	.....	.....	.....	58.0	42.0	1,200	1,400	1	.00	15.6	196	196	195	3,600	1,900	1,100

The range in composition of the specimens is illustrated by the diagram in figure 1.[4] Some of the preparations with compositions indicated by points on the join $3SrO:2TiO_2$–$BaO.TiO_2$(fig. 1), even though mature, disintegrated after several months storage in porous paper envelopes. As stability of capacitors after prolonged exposure to moisture in the air is important, several specimens of $SrO.TiO_2$ and those with compositions represented by points on the $BaO.TiO_2$–$SrO.TiO_2$ join were remeasured for K and Q after storage under room conditions for 6 months or more. The values of K and Q had not changed,which indicated that no disintegration had occurred.

Two objects of the heat treatments were (1) to expel the CO_2 from the carbonates, and (2) to induce reactions among the remaining oxides so that mature specimens (less than 0.10 percent of absorption) resulted. Although a single heat treatment sufficed for a few preparations, a preliminary heat treatment for calcining most of the batches was necessary. One advantage of calcination was the elimination of difficulties experienced in dry-pressing disks from the extremely fine-grained original materials.

In calcining the batches, a relatively high temperature was unsatisfactory. When such temperatures approached those for maturing the disks, the resulting calcines were more difficult to pulverize and to form into compact dry-pressed disks than were the calcines produced at temperatures 100°C or more below those of the final heat treatments. Possibly an objection to calcining at relatively low temperatures is the high shrinkage (10 to 20 percent) that occurs on maturing. Such an objection is more than offset by the ability to produce practically nonabsorbent specimens from these calcines, whereas the "high calcined" material was much more difficult to mature. In this study, over 500 disks were made because of the difficulty in finding the narrow range in temperature at which many of the specimens matured.

In the second heat treatment for preparation of mature specimens, the maximum temperature varied from 1,250°C, for $BaO:2.2\ TiO_2$, to 14,30°C for specimens with compositions in the join $BaO.TiO_2$–$3SrO:2TiO_2$ (fig. 1). Although the time at the maximum temperature of the heat treatments was varied widely, 1 to 30 hr, a duration of 1 or 2 hr was sufficient for calcining the batches and maturing the specimens. Approximate maturing temperatures are indicated in figure 2.

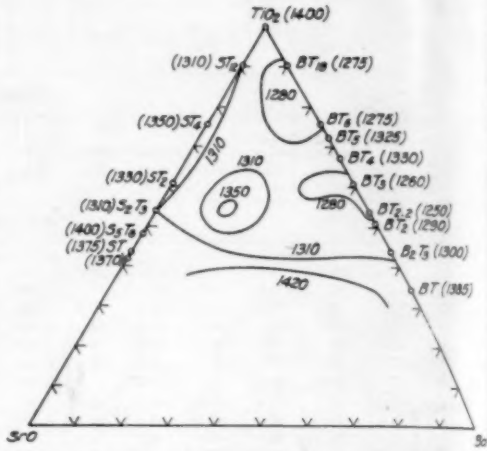

FIGURE 2.—*Maturing temperature after sintering treatment.*
B=BaO; S=SrO; T=TiO_2.

In the determination of the dielectric constant and Q, the advantage of specimens with low values of absorption (0.1 percent or less) is apparent from the data on specimens *TMO* (table 1), which are typical for all specimens studied. Although the values of K and Q decrease as the absorption increases, the amount of change in K is much less pronounced than that in Q. The values of K were duplicated usually within 1 or 2 percent, but variations of several percent in the values of Q were not uncommon.

The data in table 3 show the effect of variation in composition on the dielectric constant (K). Values of 91 to 98 for mature specimens of titania prepared from grades *TMO*, *A*, and *R*, table 1, are within the range of values obtained by other investigators [1, 2], for the dielectric constant of such material. Additions of BaO to TiO_2 resulted in (1) gradually decreasing values of K (at 25° C) from 98 to a minimum of 34 ($BaO:4TiO_2$), followed by (2) increasing values of K to a maximum of 1,500 ($BaO:TiO_2$). The values of K increased rapidly when the content of BaO was increased from 46.3 to 65.7 percent.

By contrast, additions of SrO to TiO_2 caused the values of K to increase gradually from 98 to 260

[4] The abbreviated designation of the composition of specimens is evident from a comparison of column 1 with 2 and 3 in table 3. Thus, $8T_{12}$ is an abbreviation for $8SrO:12TiO_2$.

SrO:TiO_2). Similarly, increasing values of K were observed in some specimens containing both BaO and TiO_2 when the SrO content was increased and the concentration of TiO_2 maintained constant. This is illustrated by compositions on the joins BaO:18TiO_2-SrO:12TiO_2, BaO:6TiO_2-SrO:TiO_2, and BaO:3TiO_2-SrO:2TiO_2, as shown in table 3. However, increasing the content of SrO with the concentrations of TiO_2 constant, but less than 61 weight percent, caused the values of K to increase rapidly to a peak and then to decrease. This is illustrated by compositions on the joins BaO:2.2TiO_2-2SrO:3TiO_2, 2BaO:3TiO_2-SrO:TiO_2, and BaO:TiO_2-SrO:TiO_2. At 25° C, changes in the dielectric constant ranging from 1,000 to 3,000 resulted from small alterations in the compositions in the join BaO:TiO_2-SrO:TiO_2, as shown in table 3.

The dielectric constant (K), measured at 1 *mc/s*, was affected also by the temperature of the specimens, as indicated by the data in table 4. The values for 30°, 50°, and 80° C, can be found by interpolation for most of the specimens. The smallest variations in K were observed for specimens with binary compositions in the range 61.0 to 75.6 weight percent of TiO_2 and 24.4 to 39.0 weight percent of BaO, whereas the largest variations in K were found for specimens that had compositions represented by points in the join BaO:TiO_2-SrO:TiO_2.

TABLE 4.—*Dielectric constant, at 1 mc/s, from −60° to +85° C, and temperature coefficient of dielectric constant at 0° C*

Specimen [a] designation	Values of K at (° C)													Temperature coefficient of K at 0° C
	−60°	−50°	−40°	−30°	−20°	−10°	0°	+10°	+20°	+40°	+60°	+70°	+85°	
														ppm
TiO_2(A)[b]	105.7	104.5	103.3	102.3	101.2	100.3	99.5	98.7	97.9	96.4	95.1	94.3	93.3	−850
TiO_2(R)[b]	106.2	104.9	103.6	102.5	101.5	100.4	99.3	98.6	98.0	96.8	95.5	94.0	93.6	.....
BT12	131	128	126	123.5	121.5	120	118	116.5	115	112.5	110	109	107	−1350
BBS6	90.7	89.6	88.4	87.5	86.6	85.8	85.0	84.4	83.7	82.7	81.6	81.2	80.4	−830
BT18	80.5	79.7	78.9	78.3	77.6	77.0	76.5	76.0	75.4	74.3	73.4	73.0	72.5	−750
BT4	186	180	174	168	163	159	155	152	149	143	138	135	131	−2500
BBS2	152	147	142	138	135	132	128	126	123	118	114	112	110	−2200
BBS5	88.5	86.4	84.7	83.4	82.3	81.2	80.2	79.2	78.0	76.2	74.8	74.2	73.5	−1300
BBS7	56.3	55.8	55.4	55.0	54.6	54.3	54.0	53.7	53.3	52.5	52.0	51.7	51.3	−650
BT6	46.5	46.3	46.2	46.0	45.8	45.6	45.4	45.3	45.1	44.9	44.7	44.6	44.5	−370
BBS8	43.1	43.0	42.9	42.8	42.8	42.7	42.7	42.6	42.5	42.3	42.3	42.2	42.2	−200
BT5	36.7	36.7	36.7	36.7	36.7	36.7	36.7	36.7	36.7	36.7	36.7	36.7	36.7	0
BBS8	44.0	43.7	43.5	43.3	43.1	42.9	42.7	42.6	42.5	42.4	42.3	42.3	42.2	−380
BBS9	36.8	36.8	36.8	36.8	36.9	36.9	36.9	37.0	37.0	37.2	37.3	37.3	37.4	+100
BT4	33.0	33.1	33.2	33.3	33.4	33.5	33.6	33.7	33.7	33.9	34.0	34.0	34.0	+260
BT2	255	244	233	224	214	206	200	195	189	180	171	167	162	−3000
BS1	220	207	197	190	183	178	173	168	164	156	149	146	141	−2300
BS3	160	151	145	140	135	132	128	126	123	118	114	112	109	−2400
BS4	112	108	105	103	100	98	96	94	92	89	86	84	82	−2200
BS6	92.8	89.5	86.7	84.5	82.0	80.0	78.5	77.0	76.0	73.5	71.2	70.3	69.0	−1900
BS7	78.9	76.3	74.0	72.0	70.2	68.6	67.4	66.2	65.2	63.4	61.8	61.2	60.3	−1800
BS8	55.9	54.8	53.9	53.2	52.6	52.1	51.8	51.4	51.1	50.4	50.0	49.8	49.4	−730
BS9	52.4	52.0	51.8	51.1	50.8	50.4	50.1	49.8	49.5	49.0	48.6	48.4	48.1	−640
BT3	44.6	44.5	44.5	44.4	44.3	44.3	44.2	44.1	44.1	43.9	43.8	43.8	43.7	−160
BZT3	274	262	250	240	230	221	213	207	202	193	184	179	173	−3200
BBS22	210	201	191	183	175	168	162	158	154	146	139	136	132	−3100
BBS23	230	216	203	192	183	175	167	161	155	144	134	131	126	−4100
BBS25	241	220	202	190	179	170	162	156	150	140	131	128	122	−4400
BBS26	216	198	182	170	159	151	145	140	135	127	118	115	111	−4100
BBS271	303	277	253	230	208	194	181	170	160	145	132	127	123	−5900
BBS279	288	292	296	297	293	284	269	246	226	187	162	152	141	.....
BBS28	227	234	239	243	249	252	254	256	256	247	226	214	190	.....
BBS29	174	181	185	192	196	198	201	204	207	216	225	231	230	.....
BT2.2	85.2	86.6	88.0	89.3	90.8	92.0	93.2	94.1	95.1	96.8	98.5	99.5	101	+1200
BT2	163	168	173	177	182	187	192	196	200	204	210	214	221	+2600

See footnotes at end of table.

TABLE 4.—*Dielectric constant, at 1 mc/s, from −60° to +85° C, and temperature coefficient of dielectric constant at 0° C—C*

Specimen [a] designation	Values of K at (° C)												Temperature coefficient of K at 0° C
	−60°	−50°	−40°	−30°	−20°	−10°	0°	+10°	+20°	+40°	+60°	+70°	+85°	
														ppm
S5T6	340	320	305	290	275	265	257	250	243	227	215	208	200	
3ST	231	222	214	206	200	194	189	184	181	173	166	163	158	
7ST	360	342	325	312	300	289	279	269	262	244	231	224	215	
ST	367	345	330	315	300	290	280	270	261	246	232	226	219	
B2S1	382	359	340	324	309	295	282	271	260	241	226	221	213	
B2S2	479	442	412	386	362	341	320	304	289	270	250	242	229	
B2S3	560	505	460	425	395	370	350	330	317	290	267	258	245	
B2S4	825	710	630	570	520	475	435	405	385	345	310	295	280	
B2S5	1290	1080	940	820	720	640	570	520	470	420	370	350	320	
B2S6	1760	1650	1480	1270	1090	970	860	780	700	575	490	450	410	
B2S72	1160	1190	1200	1210	1200	1180	1130	1080	1015	825	675	610	530	
B2S83	920	950	980	1010	1025	1045	1055	1070	1085	1090	980	910	800	
B2S9	735	775	810	845	880	910	940	970	995	1055	1120	1155	1125	
B2S95	610	640	670	700	730	755	780	805	825	870	920	945	980	
B2T3	600	630	660	690	720	745	780	825	870	900	920	935	980	
SB9	466	424	397	381	348	343	325	313	303	283	264	256	247	
SB79	622	565	520	485	450	422	397	380	362	332	306	297	279	
SB72	827	755	690	635	580	535	500	460	430	385	345	330	311	
SB64	1415	1210	1020	870	770	650	630	580	535	470	420	395	367	
SB57	3000	2150	1500	1210	1020	850	780	710	645	550	480	450	410	
SB50	13400	6300	3700	2400	1850	1450	1200	1020	925	750	625	580	520	
SB39	3300	3450	4000	5800	11500	7200	4000	2500	1900	1270	950	850	740	
SB34	3720	3640	3800	4200	5400	12000	10000	5000	3600	2000	1370	1170	970	
SB32	3340	3300	3300	3400	3800	5700	15000	11000	6000	2450	1550	1320	1070	
SB29	2180	2370	2400	2400	2450	2800	3600	10000	8500	3200	1820	1370	1190	
SB26	1970	2230	2750	2750	2750	2750	3200	8000	13800	4700	2360	1850	1420	
SB23	1240	1400	2180	2060	1980	1980	2020	2300	3000	7500	3100	2400	1720	
SB21	1450	1700	2570	2450	2350	2350	2350	2350	2600	11000	4800	3500	2170	
SB18	1250	1400	1600	1850	2150	2150	2050	2100	2200	3100	8500	5200	3200	
SB16	940	1050	1250	2000	1850	1710	1650	1650	1700	2050	7300	6500	3740	
SB1	780	830	900	950	1100	1700	1600	1500	1450	1410	1600	2050	8200	
BS37	1670	1800	2270	2000	1600	1350	1100	950	820	690	560	500	435	
BS375	2330	2400	2600	2800	3650	4000	3080	2300	1850	1270	920	820	690	
BS38	1290	1650	1950	2050	2100	2150	2300	2600	3300	4320	2380	1950	1420	
BS39	1250	1350	1550	1800	2450	2400	2300	2250	2200	3000	7500	6000	2100	
BT	805	815	860	910	980	1060	1160	1310	1570	1360	1300	1330	1440	

[a] For compositions, see tables 1 and 3.
[b] Grade designation (table 1).

The effect of temperature, over the range −60° to +85° C, upon the dielectric constant of specimens in the system BaO-TiO_2 is illustrated by figure 3. In diagram *A* the negative temperature coefficient of K for titanium dioxide is indicated by the curve TiO_2. It is seen that increasing the content of BaO in the specimens (to approximately 28 weight percent), as in BaO:$5TiO_2$, resulted in a reduction of the negative temperature coefficient. Attention is directed to the specimen containing 27.7 percent of BaO, because the dielectric constant remained unaltered by changes in temperature within the range −60° to +85° C, as shown by the curve BaO:$5TiO_2$. Certain irregularities in the dielectric constant appeared when the concentration of BaO was more than 28 weight percent. Specimen BaO:$4TiO_2$ (32.4 percent of BaO) had a slightly positive temperature coefficient of K as well as the lowest observed value for K, as shown by the curve BaO:$4TiO_2$ in diagram *A*, figure 3. A further increase of 6.6 percent of BaO resulted not only in a higher value of K but also in a slightly negative temperature coefficient, as illustrated by curve BaO:$3TiO_2$ in diagram *B*. As the concentration of BaO increased within the range 39 to 65.7 weight percent (BaO:$3TiO_2$ to BaO.TiO_2) the dielectric constant of the specimens exhibited more pronounced changes with temperature as well as increased values of K, as illustrated by

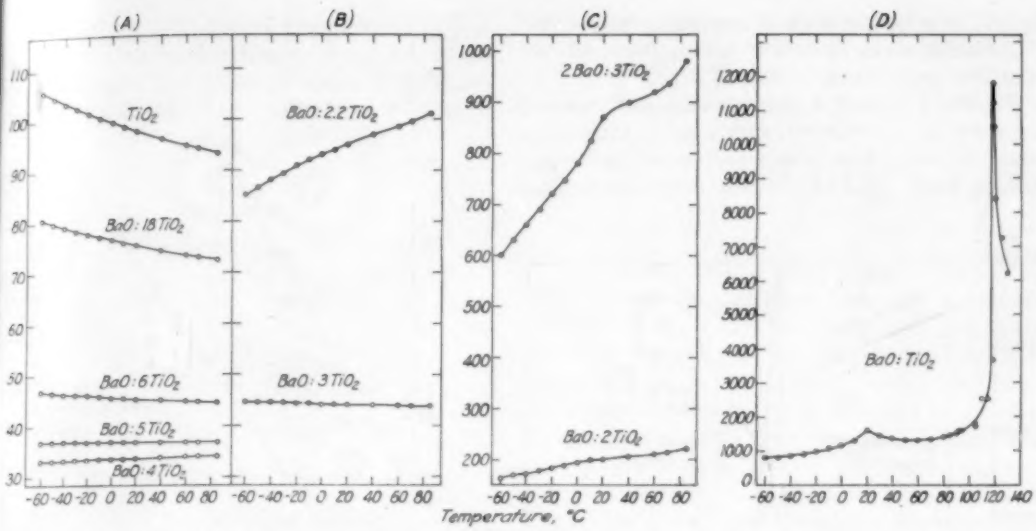

FIGURE 3.—*Variation of dielectric constant with temperature, at 1,000 kc/s, for specimens with compositions in the binary system,* TiO_2–$BaTiO_3$.

diagrams *B*, *C*, and *D* (fig. 3). It should be noted that the scales were altered in the ordinate of diagrams *C* and *D*, because of the high values of *K*.

Other investigators [1, 2] have found considerable variation in dielectric constant with changes in temperature of specimens prepared from $BaO.TiO_2$. In the present study, diagram *D*, figure 3, shows the character of the dielectric-constant–temperature curve for these specimens. Although a peak value of 11,800 *K* was observed at 118° C, variations of as much as 1,000 or more in the values of *K* were caused by small changes in temperature within the range of 110° to 125° C. The rapid variation of *K* with temperature occurs at a reversible change in crystal structure from pseudocubic to the cubic perovskite structure [2], indicated by X-ray studies.

Additions of SrO to specimens containing BaO and TiO_2, denoted by the joins in the diagram of figure 1, resulted in negative temperature coefficient of *K* for most of the specimens, as shown in the last column of table 4. Coefficients were not computed for all the specimens because of the irregularities in the curves of dielectric constant versus temperature.

The portion of the ternary diagram in which peaks were observed in the dielectric-constant—temperature curves is indicated in figure 4. These peaks were a maximum for specimens with compositions indicated by points in the join $BaO.TiO_2$-$SrO.TiO_2$. The curve with a peak at 41° C (fig. 5) for one of these specimens, *SB21*, resembles the curve for $BaO.TiO_2$ (fig. 3, *D*). It was found that increasing the content of SrO in this series of compositions on the $SrO.TiO_2$-$BaO.TiO_2$ join resulted in decreasing the temperature at which the peak in dielectric constant occurred (fig. 6). Extrapolation of the curve indicates a peak for

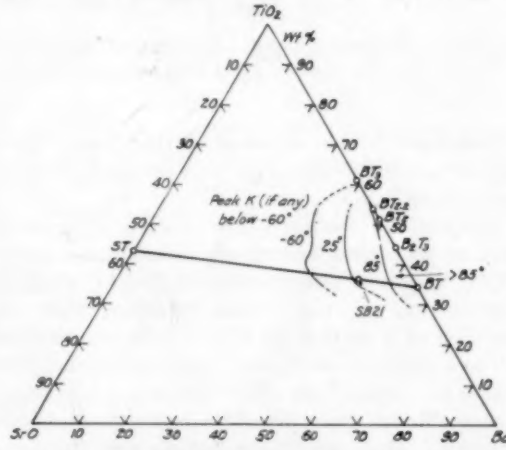

FIGURE 4.—*Relation between the temperature at which the peak dielectric constant occurs and compositions in the* BaO-SrO-TiO_2 *system.*

B = BaO; S = SrO; T = TiO_2.

$SrTiO_3$ at a temperature of approximately −240° C. Similar data by other investigators indicate that this peak is near −260° C [7].

Figures 7, 8, and 9 show the lines of constant values of K at −60°, 0°, and +60° C with variations in composition over a portion of the ternary system BaO-SrO-TiO_2. These diagrams indicate

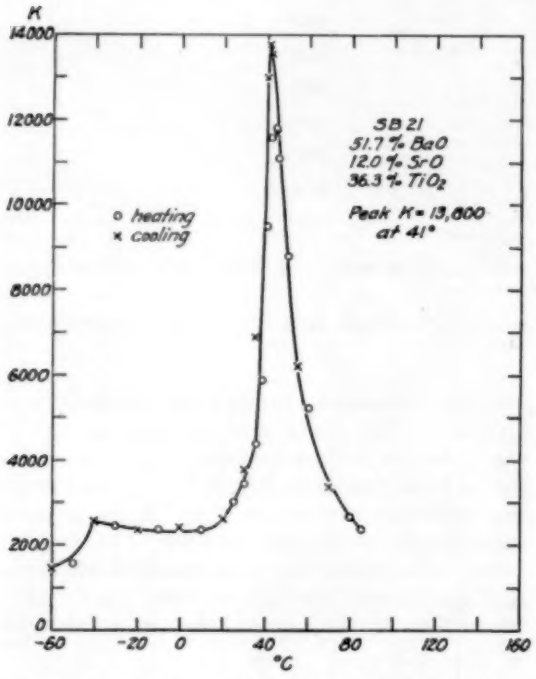

FIGURE 5.—*Variation of dielectric constant with temperature, at 1,000 kc/s, for specimen SB21 with composition on the* $SrTiO_3$-$BaTiO_3$ *join.*

the changes in the values of K that result from simultaneous alterations of both temperature and composition.

Despite the relatively low dielectric constant (37) of specimens having the composition BaO: $5TiO_2$, the zero temperature coefficient of K is noteworthy. It was found, however, that an addition of 5 percent of SrO to this composition led to a negative coefficient, as in specimens 5BS8 (table 4). Specimens 4BS8 also had a low negative coefficient, whereas 4BS9 had a positive coefficient. Thus, specimens having zero temperature coefficient of K are limited in composition to a small region in the vicinity of the composition indicated by the point BT5, figure 1. For some

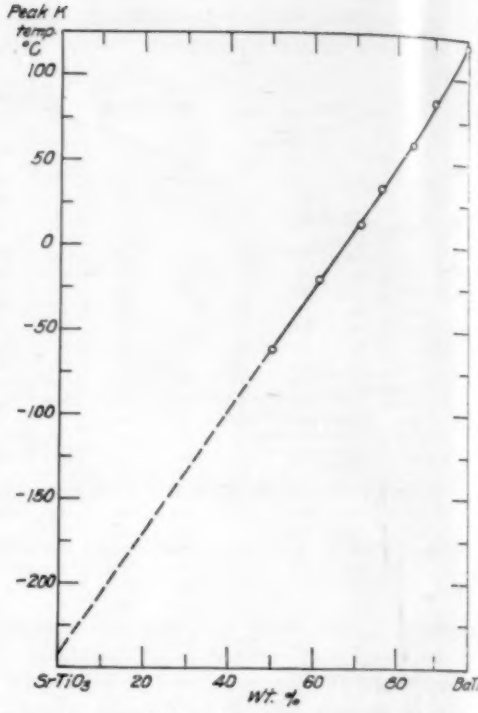

FIGURE 6.—*Variation of the temperature at which the peak dielectric constant occurs with composition on the* $SrTiO_3$-$BaTiO_3$ *join.*

uses, such as delay lines, the dielectric with zero temperature coefficient is desirable.

The dielectric constant was not affected by variations in frequency within the range 50 to 20,000 kc/s. It is believed that the slight differences in observed values of K are within experimental error.

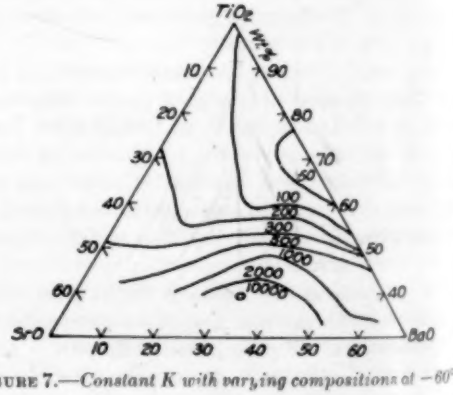

FIGURE 7.—*Constant K with varying compositions at* −60° C

The variation in values of Q caused by alterations in composition and frequency is shown by the data in table 3. Although most of the specimens had relatively high values of Q (400 to

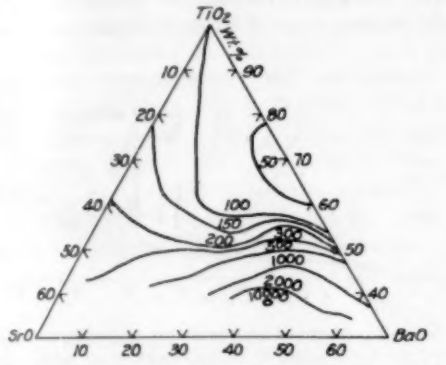

FIGURE 8.—*Constant K with varying compositions at 0° C.*

10,000), those containing more than 46.0 percent of BaO exhibited low values of from 50 to 100. With specimens having a constant and relatively low content of TiO_2, an increase in the concentra-

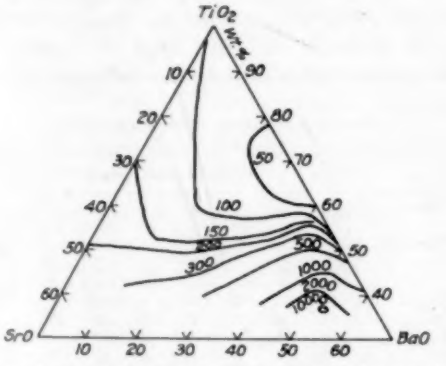

FIGURE 9.—*Constant K with varying compositions at +60° C.*

tion of SrO was accompanied by increased values of Q, as illustrated in table 3. As an absorption of over 0.01 percent was attended by a lower value of Q, some of the specimens with absorptions over 0.01 percent probably exhibited values of Q lower than the best obtainable.

TABLE 5.—*Dielectric constant K, and Q, the reciprocal of the power factor, at 25° C and 1 mc/s and 3,000 mc/s*

Specimen designation	K at 1 mc/s	Q at 1 mc/s	K at 3,000 mc/s	Q at 3,000 mc/s
BaO: $3TiO_2$	43	3,600	42	460
B86	75	2,400	76	520
B87	71	1,000	74	310

The data in table 3 show little correlation of Q with frequency. In some instances, a specimen had low Q at 50 kc/s and fairly high Q at 20,000 kc/s, for example, *BT*6. Often a duplicate specimen exhibited a high Q at all frequencies. As an example of the variation in Q values of specimens receiving the same preparation and heat treatments, the data in table 6 are given. Although the variation in the dielectric constant is not large, the Q values show a very large variation. However, the specimen with the highest absorption has the lower Q value. The reason for these differences is not apparent, but it may be connected with a number of factors, such as the size of crystals and pores, as well as the state of oxidation of the titanium compounds.

Variations in the properties of specimens of the same composition, *SB*50, which received different heat-treatments, are given in table 7. These specimens have a fairly large maturing range with small variation in dielectric constant. Similar data could be given for most of the other compositions of low BaO content.

TABLE 6.—*Properties of specimens of* $SrTiO_3$, *sintered for 1 hr at 1,245° C and heated at 1,350° C for 1 hr*

Absorption	Shrinkage	Dielectric constant (K), 25° C			Reciprocal (Q) of power factor, 25° C		
		50 kc/s	1,000 kc/s	20,000 kc/s	50 kc/s	1,000 kc/s	20,000 kc/s
Percent	*Percent*						
0.11	14.8	268	264	260	450	1,350	3,500
0.06	15.0	249	246	243	2,100	3,200	4,800
0.05	15.0	258	254	249	900	4,000	8,000
0.05	14.8	253	250	245	1,000	1,350	4,500
0.01	15.2	260	260	260	5,500	8,000	10,000
0.00	15.0	252	249	245	900	4,000	8,000

TABLE 7.—*Properties of specimens of SB50, sintered at 1,245° C for 1 hr, and heated at 1,350° C, 1,385° C, and 1,420° C for 2 hr*

Heated 2 hr	Absorption	Shrinkage	Dielectric constant (K), 25° C			Reciprocal (Q) of power factor, 25° C		
			50 kc/s	1,000 kc/s	20,000 kc/s	50 kc/s	1,000 kc/s	20,000 kc/s
° C	*Percent*	*Percent*						
1,350	0.02	14.3	870	900	860	2,900	6,100	1,600
1,350	.05	14.3	870	890	900	3,400	5,800	1,300
1,385	.05	14.2	870	870	890	5,400	7,000	1,600
1,385	.07	14.3	870	870	890	5,700	7,500	1,400
1,420	.01	14.3	860	860	870	2,800	8,500	1,700
1,420	.02	14.3	870	860	870	2,300	7,500	1,200

In the specimens having a high BaO content, and low Q values, the variations in the dielectric constant and the Q values are more nearly equal, as shown by the data in table 8. In general, for specimens having a low BaO content, the variations in the dielectric constant, for well vitrified samples, are much less than the variations in the Q values, although for specimens of high BaO content, and low Q values, these variations are more nearly equal.

TABLE 8.—*Variations in properties of some specimens containing over 40 percent of BaO*

Specimen designation	Heat treatments				Absorption	Dielectric constant (K), 25° C			Reciprocal (Q) of power factor		
	Temperature	Time	Temperature	Time		50 kc/s	1,000 kc/s	20,000 kc/s	50 kc/s	1,000 kc/s	20,000 kc/s
	° C	*hr*	*° C*	*hr*	*Percent*						
SB16	1,245	1	1,375	2	0.00	1,930	1,850	1,810	33	74	60
	1,245		1,385	2	.05	1,890	1,840	1,820	36	112	62
	1,245		1,420	2	.60	1,920	1,850	1,790	36	119	62
B_2S95	1,200	1	1,310	2	.05	860	830	820	83	61	28
	1,200		1,285	2	.00	840	820	810	74	52	27
BT	1,245	1	1,385	2	.05	1,460	1,410	1,360	79	93	50
	1,245		1,425	2	.08	1,480	1,480	1,410	82	84	44
Bt [a]	1,245		1,400	1	.03	1,660	1,650	1,670	134	74	28
Bt [b]	1,245				1.07	1,330	1,300	1,330	98	144	78

[a] $BaTiO_3$ made with TiO_2, grade *WD*.
[b] $BaTiO_3$ made with TiO_2, grade *R*.

Coating the specimens, particularly those having relatively high absorption, with wax or paraffin increased the values of Q. The improvement, however, was not permanent, for on standing a gradual decrease in Q was noted.

At a frequency of 3,000 mc/s, a greater difference was observed in the values of Q than of K compared with their respective values found at a frequency of 1 mc/s, as indicated by the data in table 5. As most specimens had a dielectric constant that was too high for determination by this method, only these three specimens were measured at 3,000 mc/s.

The thermal expansion of the specimens was high, ranging from 0.59 to 0.84 percent between

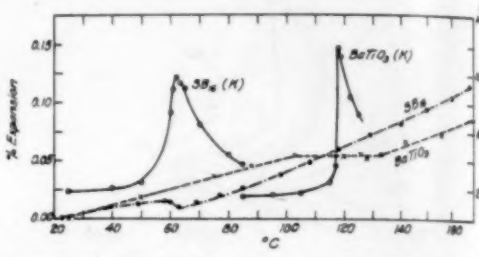

FIGURE 10.—*Thermal expansion for a specimen of* $BaTiO_3$ *and for SB16 (table 3) in the region of the peak dielectric constant, over the range 25° to 170° C.*

Solid lines for dielectric constant and broken lines for thermal expansion.

room temperature and 700° C, despite the wide variation in composition (table 9). Figure 10 illustrates a peculiar feature of the expansion curve for specimens with compositions in the join $BaO:TiO_2$-$SrO:TiO_2$. The flat section of these curves occurred in the range of temperature characterized by a peak in the dielectric constant.

TABLE 9.—*Linear thermal expansion*

Specimen designation	Temperature range from 25° C to—								
	100° C	200° C	300° C	400° C	500° C	600° C	700° C	800° C	900° C
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
TiO_2	0.06	0.14	0.23	0.32	0.41	0.50	0.60	0.69	0.78
BT18	.05	.14	.23	.31	.41	.50	.59		
BT6	.05	.14	.24	.33	.43	.54	.64		
BT5	.06	.15	.24	.34	.45	.57	.68		
BT4	.06	.14	.23	.32	.41	.51	.60	.70	
BT3	.06	.16	.26	.37	.48	.59	.71		
BT2.2	.06	.16	.26	.37	.49	.61	.72		
BT2	.07	.16	.28	.40	.52	.65	.78		
BT	.05	.13	.25	.38	.52	.66	.80		
SB64	.07	.18	.30	.42	.55	.67	.80		
SB29	.07	.19	.32	.44	.58	.71	.84		
SB29F [a]	.07	.19	.29	.41	.54	.68	.79		
SB16	.04	.16	.28	.41	.55	.68	.81		
ST	.07	.17	.29	.40	.51	.63	.74		
ST2	.06	.16	.26	.36	.46	.55	.65	.75	
ST4	.06	.15	.25	.35	.44	.55	.65		

[a] 3% MgF_2 added.

Although the construction of a phase diagram for this system was outside the scope of this investigation, there were indications, based on

maturing temperatures, of the existence of compounds in various regions of the diagram, figure 2. For example, a binary compound in the region of $BaO{:}4TiO_2$ is suggested by the maturing temperature, dielectric constant, and X-ray spectrogram. In fact, a comparison of X-ray patterns for all the specimens in the system $BaO\text{-}TiO_2$ indicated the formation of other compounds in addition to $BaO{:}4TiO_2$ and $BaO{:}TiO_2$.[5] The maturing temperature of 1,350° C for specimens in the region 18 percent BaO, 28 percent SrO, 54 percent TiO_2 is suggestive of a ternary compound, but the suggestion is not supported by data on the dielectric constant or by X-ray patterns.

V. Conclusions

Mature specimens (absorption less than 0.10 percent) can be made from mixtures of titanium dioxide with barium and strontium carbonates, which have compositions represented by points in the system $BaTiO_3\text{-}SrTiO_3\text{-}TiO_2$. The dielectric constant of these specimens varies from 34 to several thousand, whereas the Q values vary from about 50 to several thousand. Most of these specimens exhibit a large negative temperature coefficient of dielectric constant, which is not too great in some to prevent their use as bypass and coupling condensers. A few have positive temperature coefficients, although that of one specimen ($BaO{:}5TiO_2$) is practically zero. When properly fabricated, some of these titanate bodies could be used also as filter or storage condensers, and as delay lines for microwave signals.

[5] The authors are indebted to H. F. McMurdie for the X-ray spectrograms and their interpretation.

VI. References

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Determination of Small Amounts of Carbon Monoxide in Air by Various Reference Methods

By Martin Shepherd

This is a report of the cooperative analyses of two samples of carbon monoxide in air. The analyses were made by laboratories engaged in investigations for the military services during the past war, and this work served to bring the results of these laboratories into common agreement.

I. Object of the Investigation

This work was undertaken to insure satisfactory accuracy of analytical results obtained by various laboratories using different fundamental reference methods for the determination of small amounts of carbon monoxide in air. As these reference methods are used to establish the composition of atmospheres in many researches dealing with the hazards, detection, and estimation of carbon monoxide, it is obviously necessary that essential agreement should exist between the different methods and the different laboratories engaged in such work. The cooperative analyses of identical samples has always been the most direct and successful way of measuring significant disagreement between different laboratories and different methods and of ultimately establishing satisfactory agreement. This approach was used in the present instance.

II. Preparation of Samples

The standard samples were prepared by the pressure-dilution method, which is well adapted to mixtures wherein one or more components are of relatively low partial pressure.

The apparatus used to prepare the standard samples was essentially a manifold with valves arranged so that connections between pressure gages, manometer, vacuum pump, and cylinders could be made in any desired combination. The valves were of the diaphragm-packless type or the Stimson [1] type and were vacuum-tight across seat, diaphragm, or (in the case of the Stimson valves) through the packing. The gages were of the laboratory-test type, carefully calibrated to the nearest 2 lb/in.^{2} and good to 4 lb/in.^{2} over the range 0 to 2,000 lb/in.^{2} Two such gages were always connected for pressure readings. The mercury-filled manometer was of the barometric type, of 20-mm bore, and was read with a cathotometer. The vacuum pump was of the regular commercial type capable of reducing the pressure to approximately 0.001 mm of mercury. Cylinders selected for this work were standard hydrogen steel cylinders (ICC 3A2015) and were equipped with diaphragm-packless valves that upon test were tight across the seat. The cylinders had previously been chained and brushed clean before inserting the valves and were dried by alternate evacuation and flushing with dried air.

It is obvious that some mixtures cannot be stored in steel cylinders; but mixtures of carbon monoxide in air, in the range of carbon monoxide desired for physiological work, do not change significantly over long periods when maintained under pressure. This fact has been carefully determined by periodically comparing samples of different ages. Comparisons were made over 2 years' duration with the NBS colorimetric method (laboratory procedure), capable of differentiating to 0.0002 percent by volume in the low concentrations studied. The samples submitted for the analyses reported herein were not stored longer

[1] Designed by Harold Stimson of the Bureau.

than 4 months before the actual analyses were made.

The whole system, as connected for each specific procedure, was tested for leaks by evacuation and/or measurement of positive pressure over a definite period within the significance required. The apparatus was located within a laboratory where the variation in temperature does not exceed 1 deg C at any time.

The procedure for preparing a standard mixture of carbon monoxide in air (actually air with a small amount of additional nitrogen) was as follows. Carbon monoxide of known purity was transferred to a cylinder by alternate evacuation and flushing. The pressure of this carbon monoxide was adjusted to the existing measured barometric pressure. Compressed nitrogen was then admitted to the cylinder until the gage registered 99 existing atmospheres, after the heat of compression had been dissipated and the cylinder was in thermal equilibrium with the room. This resulting mixture, which was very close to 1 percent carbon monoxide, was diluted in the same manner, but with air, until its concentration had been reduced to 0.0100 percent, or to some desired value of this order.

The gases under pressure were thoroughly mixed by thermal convection. The cylinder was inclined to about 45 degrees, and the top was cooled while the bottom was heated for about 24 hours. Water from the cold and hot taps (about 15° and 65° C, respectively) served for this purpose.

The composition of the mixture with respect to carbon monoxide was computed from the equation

$$\text{Percentage of CO} = M_{CO} \frac{P_{CO}}{760} \frac{14.696}{P_G + 14.7} \frac{R_2}{R_1} \frac{T_2}{T_1},$$

in which

M_{CO} = percentage of carbon monoxide in the gas taken for dilution

P_{CO} = initial pressure of carbon monoxide or of a subsequent mixture of carbon monoxide with air, taken for dilution. (This is the existing barometric pressure in mm Hg, before dilution.)

P_G = final gage pressure in lb/in.^{2}

R_1 = value of PV/nRT for carbon monoxide (or N_2 on the second dilution) at 1 atm and temperature T_1

R_2 = value of PV/nRT for air (or N_2) a the pressure P_G and temperatur T_2

T_1 = initial cylinder temperature (° (abs.)

T_2 = final cylinder temperature (° (abs.).

The carbon monoxide used to prepare the tw standard samples was analyzed by the apparatu and methods described by J. R. Branham, M Shepherd, and S. Schuhmann [1].[2]

The analysis was

CO	97.94 percent by volume.
H_2	2.03 percent by volume.
Fe $(CO)_5$	0.03 percent by volume.

The Fe $(CO)_5$ was determined by condensing thi substance from a measured large volume o sample, at approximately −160° C, in a condense equipped with glass-wool filter, and determinin the iron.

This reference method as described and cor rected is good to less than 0.1 percent by volum of carbon monoxide. The pressures measured wer good to 4 lb/in.^{2} (0.2 percent at maximum pres sure). The temperatures were measured to 0. deg C. The maximum over-all uncertainty in pre paring such mixtures at near the maximum operat ing pressures is about 0.0001 percent of carbo monoxide, and the probable uncertainty is less.

In the case of the two samples considered in thi report, Sample 1 serves for a study of reproduc ibility and sample 2 for a study of both accuracy and reproducibility. When the samples wer issued for analysis, it was thought that the com position of both was known to the desired signifi cance, but review of the preparation of the firs sample places too great an uncertainty upon it composition, and accordingly it will serve only a a means of showing the degree of reproducibility to be expected in the approximate range of 0.03 percent of carbon monoxide.

The standard samples were transferred to smaller cylinders for distribution to the various labora tories. This was done by connecting the large cylinder containing a standard sample and the small cylinders to a manifold. The whole system was evacuated and tested for tightness. Prior to the final filling under high pressure, the smal

[2] Figures in brackets indicate the literature references at the end of th paper.

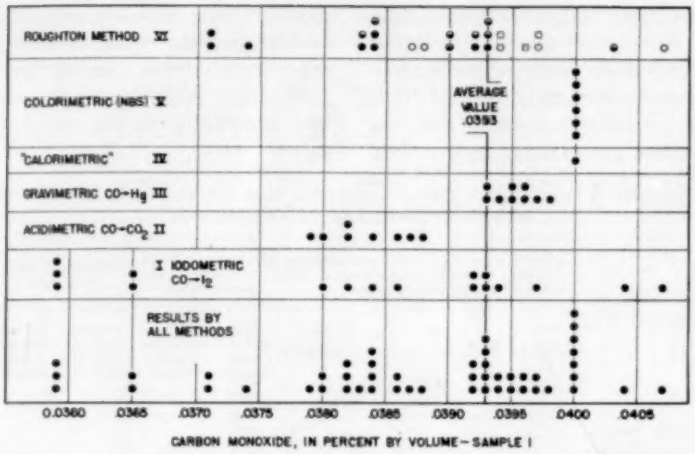
ROUGHTON METHOD XI
COLORIMETRIC (NBS) V
AVERAGE VALUE .0393
"CALORIMETRIC" IV
GRAVIMETRIC CO→Hg III
ACIDIMETRIC CO→CO2 II
I IODOMETRIC CO→I2
RESULTS BY ALL METHODS
0.0360 .0365 .0370 .0375 .0380 .0385 .0390 .0395 .0400 .0405
CARBON MONOXIDE, IN PERCENT BY VOLUME—SAMPLE 1

FIGURE 1.—*Frequency-distribution plot for the analysis of a known sample of carbon monoxide in air.*

cylinders were alternately evacuated and flushed with the standard sample.

The laboratories were thus assured of receiving identical samples.

III. Analytical Results

The two samples were submitted as unknowns, and no cooperating laboratory was given information concerning their composition other than the general statement that the mixtures were carbon monoxide in air. The results were reported directly to the Bureau and have been assembled for general study. Some really fine analytical work has been reported.

The analytical results are tabulated (table 1) and are also presented in two frequency-distribution plots, one for each sample (figs. 1 and 2). These plots show graphically the major facts to be derived from the analytical data. Each point or circle of the frequency-distribution plots represents the amount of carbon monoxide found by a single analysis, corrected by whatever factor

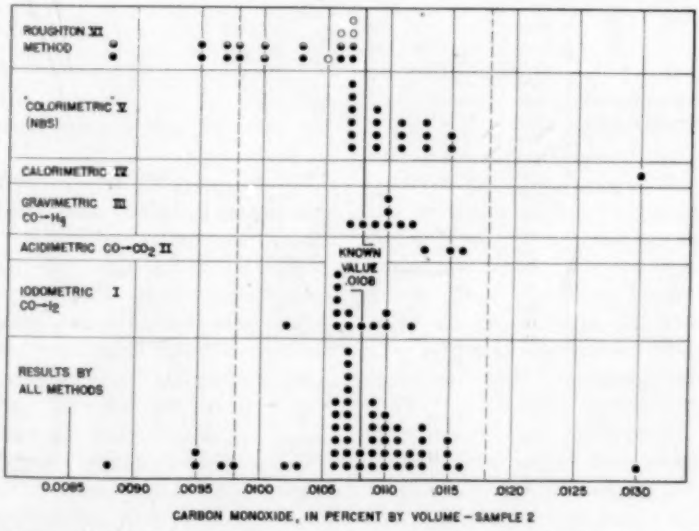
ROUGHTON XI METHOD
"COLORIMETRIC" V (NBS)
CALORIMETRIC IV
GRAVIMETRIC III CO→Hg
ACIDIMETRIC CO→CO2 II
KNOWN VALUE .0108
IODOMETRIC I CO→I2
RESULTS BY ALL METHODS
0.0085 .0090 .0095 .0100 .0105 .0110 .0115 .0120 .0125 .0130
CARBON MONOXIDE, IN PERCENT BY VOLUME—SAMPLE 2

FIGURE 2.—*Frequency-distribution plot for the analysis of a known sample of carbon monoxide in air.*

was furnished by the reporting laboratory. The circles are plotted equidistant on the ordinate corresponding to their value. Thus, the abscissas are percentages of carbon monoxide derived from the analyses, and the ordinates indicate the frequency with which these percentages occur. For example, the plot for sample 1 (fig. 1), bottom section (results by all methods) shows that seven separate analyses yielded the value 0.0400 percent, one analysis gave the value 0.0398 percent, two analyses gave the value 0.0397 percent, and so on.

TABLE 1.—*Cooperative analysis of two Standard Samples of carbon monoxide in air, by reference methods used in various laboratories working for the Armed Forces*

Laboratory number	Analytical method	Carbon monoxide found (percentage by volume)		Corrected averages (percentage by volume)		Deviations of the corrected averages from—		Maximum deviations from—		Notes regarding the nature of the corrections, etc.
		Sample 1	Sample 2	Sample 1	Sample 2	Average composition of sample 1	Known composition of sample 2	Average composition of sample 1	Known composition of sample 2	
1	Iodometric, based on Graham method, using the AGA apparatus.	0.0359	0.0106							Average of 3 analyses (value 0.0359).
		.0365		0.0361	0.0106	−0.0032	−0.0002	(a)	(a)	Average of 2 analyses (value 0.0365).
2	Iodometric—Graham procedure, with desiccblora, silica gel, Ascarite, P_2O_5, I_2O_5 at 160° C, 3% KI solution.	.0384	.0108							Two trains employed.
		.0392	.0107							
		.0393	.0102							
		.0394	.0106	.0391	.0106	−.0002	−.0002	0.0009	0.0006	
3	Iodometric—Goldman and Brandt Am. J. Public Health **32**, 475 (1942).	.0380	.0107							
		.0386	.0112							
		.0391	.0106		0108				.0004	
		.0404								
		.0407								
		.0397		.0394		+.0001	0	.0014		
		.0382	.0106							
4	Iodometric	.0391	.0109	.0386		−.0007		.0011		
			.0110							
			.0110		.0109		+.0001		.0002	
5	Oxidation of CO over Hopcalite at 100° C, absorption of CO_2 in barium hydroxide and acidimetric determination.	.0380	.0105							Values include an indicator blank of 0.001.
		.0384	.0106							
		.0379	.0103		.0115		+.0007		.0008	
		.0382								
		.0382								
		.0387								
		.0388								
		.0384		.0383		−.0010		.0014		
6	Reduction of mercuric oxide and gravimetric determination of the mercury lost.	.0395[1]	.0111[1]							Average includes a blank correction of −0.000.
		.0393[2]	.0108[2]							
		.0395[3]	.0111[2]							
		.0398[4]	.0109[3]							
		.0397[4]	.0110[3]							
		.0394[3]	.0111[3]							
		.0398[5]	.0112[7]							
		.0396[6]	.0109[4]		.0110		+.0002		.0006	
		.0396[4]		.0395		+.0002		.0007		
7	Calorimetric	.040	.013	.040	.013	+.0007	+.0022	.0007	.0022	1 measurement.
8	NBS colorimetric laboratory method.	.040	.0107							
		.040	.0109							
		.040	.0113							
		.040	.0115							
		.040	.0107							
		.040	.0109	.040		+.0007		.0007		
			.0107							
			.0107							
			.0107							
			.0109							
			.0107							
			.0111							
			.0113							
			.0115							
			.0109							
			.0113							
			.0111							
			.0111		.0110		+.0002		.0007	

[a] Not known.

TABLE 1.—*Cooperative analysis of two Standard Samples of carbon monoxide in air, by reference methods used in various laboratories working for the Armed Forces*—Continued

Laboratory number	Analytical method	Carbon monoxide found (percentage by volume)		Corrected averages (percentage by volume)		Deviations of the corrected averages from—		Maximum deviations from—		Notes regarding the nature of the corrections, etc.
		Sample 1	Sample 2	Sample 1	Sample 2	Average composition of sample 1	Known composition of sample 2	Average composition of sample 1	Known composition of sample 2	
9	Roughton method	0.0377	0.0098	0.0377	0.0098	−0.0016	−0.0010	(a)	(a)	Individual determinations not reported.
		.0384	.0106							
		.0371	.0103					0.0022		Values first reported.
		.0374	.0098							
		.0371	.0088						0.0020	
		.0383	.0095							
		.0393	.0097							
		.0392	.0095							
		.0384	.0107	.0382	.0099	−.0011	−.0009			
10	Roughton method, which includes absorption of CO in blood, subsequent removal therefrom by Van Slyke procedures, and final determination by absorption in ammoniacal cuprous chloride in a Scholander-Roughton micropipette. Four sets of results were submitted. (See remarks.)	.0403	.0106							
		.0390	.0103							
		.0393	.0098							First values corrected for an error found in one apparatus.
		.0390	.0088						.0020	
		.0383	.0100					.0010		
		.0393	.0097							
		.0392	.0100							
		.0384	.0107	.0391	.0100	−.0002	−.0008			
		.0407	.0106							
		.0394	.0103							
		.0397	.0098							Corrected values corrected for excess of nitrogen in the sample over the amount in air.
		.0394	.0088							
		.0387	.0100					.0006	.0020	
		.0397	.0097							
		.0396	.0100							
		.0388	.0107	.0393	.0100	0	−.0008			
			.0105							Results from the improved method, which consists in using a 300-ml sample instead of a 30-ml sample.
			.0106							
			.0107							
			.0107		.0107		−.0001		.0002	

[a] Not known.

1. Sample 1

Practically the whole story of sample 1 can be seen in figure 1. The bottom section gives a picture of the distribution of analytical results by all the methods employed. Most of the results are clustered between the values 0.0380 and 0.0400, with the greatest frequency near and at the higher value. If the five low results by the iodometric method are eliminated, the arithmetical average of all other results is 0.0392; and with the highest and the lowest 10 percent of all values dropped, the average is 0.0393. This value is taken as the average result of the analyses of sample 1.

These data are in turn broken down to obtain the picture of each of the analytical methods used. The second section from the bottom of this plot gives this picture for the iodometric method (I), generally called the iodine pentoxide method [2]. Referring now to the table, it is noted from columns 1 and 2 that four laboratories used this method, with some variations, and that the five low results reported are from one of the four laboratories. The values for this method are relatively scattered and suggest the need for standardizing the actual procedures used. The average of all results by this method is 0.0383, lower than the average value by all methods; the average of all results after dropping the five low ones is 0.0392, in good agreement with the average value by all methods.

The next section of the plot gives the results reported by an acidimetric method (II) [3]. According to this method, carbon monoxide is converted to carbon dioxide by Hopcalite at 100° C, and the carbon dioxide is absorbed in barium hydroxide and determined acidimetrically. The

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results plotted are corrected for an indicator blank of 0.001. These results are well grouped and all are lower than the average value by all methods. The average is 0.0383.

The next section gives the results [4] from a gravimetric method (III) that depends upon the reduction of mercuric oxide at 175° C. Carbon monoxide is calculated from the measured loss of weight of the oxide. These results are very well clustered near the general average value, with an average of 0.0395, and leave little to be desired, even by the most exacting analysts.

The next section gives one point reported by a "calorimetric method" (IV), wherein the rise of temperature produced by the combustion on Hopcalite at 100° C is measured by a mercury-in-glass thermometer.

Section V gives values obtained by the NBS colorimetric method [5]. When CO occurs in amounts as large as 0.03 to 0.04 percent, it is estimated to the nearest 0.001 percent by this method. The apparent excellent reproducibility should accordingly not be misunderstood because the choice here was merely between 0.039, 0.040, or 0.041 percent, and the observations indicated an even 0.040 percent.

The Roughton method outlined in section VI employs the following procedures. The sample is freed from oxygen, and thereafter the carbon monoxide is absorbed by prolonged contact with blood. The blood is then freed from other gases by Van Slyke procedures in the Van Slyke manometric apparatus, and after removal of these gases, the carbon monoxide is liberated, and the final residue of carbon monoxide is transferred to a Scholander-Roughton microsyringe and there absorbed in ammoniacal cuprous chloride.

The original results obtained by this method are those indicated by the filled circles. One laboratory reported an average of 0.0377 percent, and another reported an average of 0.0382 percent. The results are badly scattered. Later the second laboratory reported an average of 0.0391, based on corrections made for an error found. These results are indicated by the half-filled circles. Still later, these results were in turn corrected because of the fact that the measurement of the sample was based upon the determination of *nitrogen* in the sample and the assumption that the sample was *air* and carbon monoxide, whereas slightly more nitrogen was actually in the sample than corresponded to the composition of air. The third set of values averaged 0.0393 (excluding the highest value) and are indicated by the open circles. The results are still somewhat scattered, though the average has finally reached the probable value, which attests to the astonishingly skillful manipulation that must have been accorded each step of this devious procedure.

2. Sample 2

Sample 2 seems to have been the inspiration for some really fine analytical work. The frequency-distribution plot for this sample appears in figure 2. Dotted boundaries have been drawn 0.001 percent away from the known value of 0.0108. The bottom section of the plot gives results obtained by all methods, and it is at once apparent that all but five of these values fall within the ± 0.001 boundaries. Indeed, most of the analyses by the five entirely different methods lie within ± 0.0005 percent of the known value, which is more than could have been hoped for.

The picture for each of the methods is given in the upper sections of this frequency-distribution plot. The values obtained by the "iodine pentoxide" method (I) do not show the wide distribution noted in the plot for sample 1. The one slightly low value was not reported from the same laboratory which gave the notably low values for sample 1. The need for standardization of this method is not so apparent in this instance. The average of all values is 0.0107, in excellent agreement with the known value 0.0108.

Acidimetric values (II) are well grouped and are all high instead of low this time. All are within the ± 0.001 boundary. The average is 0.0115.

Gravimetric values (III) are consistently grouped and all are within 0.0004 of the known value. The average, 0.0110 (0.0109_6), is slightly high. This method seems to have given the most consistent over-all performance with the low and high range of composition. The error for each sample was small, and apparently systematic. Thus, a redetermination of the blank or possibly a check of the measurement of the volume of the sample might establish an average in even closer agreement with the known value, if there is any desire to do so.

A single high point is noted for the calorimetric method (IV).

The colorimetric method (V) yielded values fairly well grouped, all within the ±0.001 boundaries, and mostly within the ±0.0005 boundaries. The fact that all values noted are odd numbers follows merely because the standard colors prepared for comparison with the unknown represented numerically even percentages, and the unknowns are, of course, placed between the standards when the color readings are made.

As before, several sets of values were reported from the second laboratory employing the physiological method, each set in succession approaching the known value more closely. The first set (closed circles) yielded an average of 0.0099 percent. (The first of the laboratories using this method reported 0.0098 percent.) The second set, corrected for a discovered error, gave an average of 0.0100 (half-closed circles). The third set, corrected for the nitrogen ratio before mentioned, did not change by a significant amount. There is also a fourth set, obtained with a 300-cm³ sample instead of a 30-cm³ sample. These determinations (open circles) yielded an average of 0.0107.

Further brief study may be devoted to the details given in the tabulated data. The data given in columns 5 and 6 are worth a moment's additional reflection. With the exception that is obviously out of line with the other data, the greatest deviation of an average value from the known value for sample 2 is 0.0009, and this includes all methods. This means that if the analyst is not inclined to take a chance with a single determination, but instead has a sufficiently healthy curiosity to perform a series of analyses, his chance of getting very close to the correct answer with any of these methods is good. If he is not too concerned with accuracy, a single determination might leave him in error by amounts varying from 0.0002 up to 0.002 percent (dropping the outside value obtained by method IV), with a good chance of his being off by no greater than 0.0008 in this range of composition.

IV. Practical Considerations

Factors like ease of manipulation, time required, complexity, cost and difficulty of maintaining apparatus, complications that may be involved in removing interfering substances, range of applicability, and such matters for practical consideration have so far not been discussed. The selection of a reference method for a particular purpose should include an appraisal from this angle, but as such matters often involve personal judgment to an embarrassing degree, no formal rating of these characteristics will be ventured. However, an informal review is in order. The following are general considerations.

1. All of the methods demand the use of known mixtures of carbon monoxide in air for calibration and regular check of performance. The colorimetric method requires the continual use of known mixtures.

2. All of the methods must make provision for interfering substances, although curiously enough, the interference in the Roughton method occurs within the analytical procedures rather than as the usual prelude to them. This comes about because blood is specific with respect to absorption of the carbon monoxide from the sample; but after this initial step, the carbon monoxide must be separated from the interfering gases in solution in the blood. Contrasted to this, the other methods are susceptible to interfering gases, such as unsaturated compounds and heavy organic vapors, that must be removed as the initial step. This is true even for the acidimetric method, for, while the catalyst used to oxidize carbon monoxide is specific for this gas, nevertheless, it is susceptible to poisoning. The removal of interfering substances is more simply accomplished with the colorimetric and gravimetric methods. (A possible exception may be the removal of hydrogen in the gravimetric method. Hydrogen does not interfere in the colorimetric method.)

3. The iodometric method requires the most complicated and costly apparatus and the one which is most troublesome to maintain in good operating order. The colorimetric method uses the simplest and cheapest apparatus and the one most easily maintained in running order.

4. The colorimetric method is not as accurate for larger amounts of carbon monoxide, unless the original sample is diluted with CO-free air. The dilution procedure will make its range comparable to that of the other methods.

5. The colorimetric method is by far the most rapid, and is by far the easiest to perform. This assumes, however, that known mixtures are available under pressure. The time spent in preparing such mixtures is not a serious factor when considering the exceedingly long life of the mixture. However, the apparatus required to prepare such

mixtures, although not expensive, must be assembled with a great deal of care, and is almost useless for any other purpose. It would accordingly be desirable to establish a suitable common source of such mixtures.

V. References

[1] Joseph R. Branham, Martin Shepherd, and Shuford Schuhmann, Critical study of the determination of carbon monoxide by combustion over platinum in the presence of excess oxygen, J. Research NBS **26,** 571 (1941) RP1396.

[2] J. Ivor Graham, The accurate determination of carbon monoxide in gas mixtures, Soc. Chem. Ind. 10–4T (1919).

[3] Cobb Chemical Laboratory, University of Virginia University, Va. (Unpublished report).

[4] Arnold Beckman, National Technical Laboratory, Pasadena, Calif. (Unpublished report.)

[5] Martin Shepherd, A preliminary report on the NB colorimetric indicating gel for the rapid determination of small amounts of carbon monoxide, Anal. Chem. **19,** 77 (Feb. 1947).

Washington, November 1, 1946.

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National Bureau of Standards

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A Magnetic-Lens Electron Spectrometer: Radiations from 5.3 Year Cobalt[60]

By Leonard C. Miller and Leon F. Curtiss

An improved magnetic-lens spectrometer, similar in principle to that described by Deutsch, Elliott, and Evans [1] has been constructed. The structure, operation, and method of calibration, using a ThB+C deposit, is described. Results of measurements of the primary beta-ray spectrum of Co^{60} and of the gamma-ray spectrum converted in a uranium radiator are given. These give an end point of 0.310 for the value reported by Deutsch, Elliott, and Roberts[2] of 0.308 $\pm$0.008 million electron volt (Mev). Two gamma rays were measured at 1.16 and 1.32 Mev, likewise in agreement with the values of 1.10 $\pm$0.03 and 1.30 $\pm$0.03 Mev, given by the same authors.

I. Introduction

An electron spectrometer for the study of radiations from radioactive substances has been constructed and put into use at the Bureau. The spectrometer is of the magnetic thin-lens type, similar in principle to that built by Deutsch [3] and his coworkers at the Massachusetts Institute of Technology. Many of the modifications incorporated in the Bureau instrument are based on those introduced by R. Wilkinson and W. Rall in the instrument they assembled at Clinton Laboratories in Oak Ridge. A description of some of these features, following that given by them in their classified report on the instrument, is included.

Radiations from 5.3 yr Co^{60} were studied as the initial work.

II. Description of the Spectrometer

The spectrometer tube consists of a cylindrical vacuum chamber. On the axis of the chamber is mounted at one end a source of radioactive material; at the other end is a thin-window Geiger-Müller counter, which acts as a detector. The lens coil is mounted coaxially with the chamber (see fig. 1). The electrons travel down the spectrometer tube, with their paths restricted by a set of baffles.

Electrons of different energies are focused on the counter window by using different currents in the lens coil. Information about the radiations from the source can then be obtained by varying the current through the coil and recording the

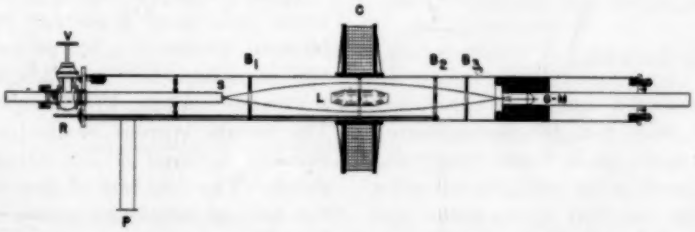

FIGURE 1.—*Longitudinal section of thin magnetic-lens spectrometer.*

B_1, B_2, fixed baffles; B_3, adjustable baffle moved from outside by rod, *R*; *C*, lens coils; *L*, lead baffle at center of lens; *P*, connection to pumps; *S*, source; *V*, gate valve with rubber gasket to close vacuum chamber. *GM*, Geiger-Müller counter with mica window.

[1] M. Deutsch, L. G. Elliott, and R. D. Evans, Rev. Sci. Instr. **15**, 178 (1944).
[2] M. Deutsch, L. G. Elliott, and A. Roberts, Phys. Rev. **68**, 193 (1945).
[3] See footnote 1.

number of counts registered by the detector at each current setting.

1. Spectrometer Chamber

The chamber consists of a brass tube 6½ in. in outside diameter, ¼-in. wall thickness, and about 6½ ft in length. The end plates are grooved and provided with rubber gaskets to make the vacuum seals. The opening through the source end plate is provided with a Wilson seal, through which passes a 1½-in. brass tube on which the radioactive source is mounted. A gate valve with a small chamber at this end, which can be evacuated, provides a means for inserting or removing sources without destroying the vacuum in the main chamber.

The opening through the end plate of the main chamber is also equipped with a Wilson seal to accommodate a 2-in. brass tube, in which the Geiger-Müller counter is mounted. The position of the detector can thus be adjusted without breaking the vacuum in the main chamber.

The pumping system consists of an oil diffusion pump backed by a Cenco Megavac pump. A pressure of about 5×10^{-5} mm of Hg can easily be attained. It was found that for most purposes a pressure of about 10^{-2} mm of Hg, attainable with the Megavac alone, was quite adequate.

The baffle system shown in figure 1 serves to define the transmitted beam and to reduce the undesirable effects due to scattering. The adjustable baffle, B_3, may be moved by means of a ¼-in. rod, R, attached to it and passing through a Wilson seal in the radiation source end plate of the spectrometer chamber. The position of this baffle affects the width of the annulus through which focused electrons pass, and thus the resolution of the instrument. The solid lead cylinders, L, on the axis of the spectrometer reduce the gamma-ray background in the counter.

2. Lens Coil

The coil was wound on a brass spool, providing a coil width of 10 cm. No. 14 glass-insulated copper wire was used, each layer containing about 52 turns. Leads were brought out to a terminal board after the first 1,326 turns, the next 1,020, the next 867, and the last 765. The coil as a whole has an inner radius of 10 cm and an outer radius of about 25 cm. Each of the four sections has a resistance of about 9 ohms, and the separate terminals to each of them provide for their use in various combinations.

During the winding, a sheet of copper of 22-mil thickness was placed over the winding every four layers. These copper sheets, 19 in all, have tongues projecting through slots in the sides of the brass spool. The tongues are soldered into brass blocks that are water-cooled. This arrangement allows for the dissipation of about 1,500 w in the coil without an excessive temperature rise in the copper winding.

3. Regulation of the Coil Current

The current for the lens coil is provided by a separate motor-generator set. This current is regulated by a method similar to that used in connection with the Berkeley cyclotron. The regulation and control circuits are shown in figures 2 and 3.

The generator field requires current up to amp. This current forms the plate current of 10 6L6 tubes connected in parallel. Regulation of the output of the generator is attained by causing the output current to control the grids of the 6L6's, as explained below.

As can be seen from figure 2, the grid voltage of the 6L6's will vary with the grid of the 6SJ7. The grid of the 6SJ7 is connected to a network containing a 920 twin-photocell tube, so that its voltage will depend on the relative illumination of the two photocells. Illumination of the photocells is provided by a galvanometer lamp, and the circuit containing this galvanometer is shown in figure 3. A double-pole, double-throw switch provides for either shorting the galvanometer or putting it into the circuit. A 1,000-ohm potentiometer provides for adjustment of the sensitivity and damping of the galvanometer.

When the galvanometer is in the circuit it is in series with the low-voltage winding of a 6.3-v filament transformer (or part of it selected by a 10K potentiometer), with a 0.001-ohm shunt, and a variable voltage, V_1, (from 0 to about 30 mv). The output current of the generator (i. e. the lens-coil current) is fed through the 0.001-ohm shunt. The direction of this current is such that the voltage developed across the shunt opposes V_1. The galvanometer coil then assumes a position determined by the balance between these two voltages.

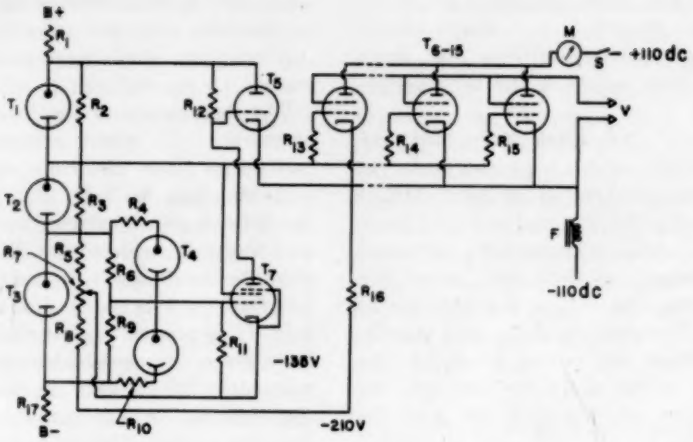

FIGURE 2.—*Diagram of circuit for stabilizing current in the lens coils of the spectrometer.*

R_{11}, R_{17}, 2,500 ohms, 10 w.; R_3, R_4, 50,000 ohms; R_6, R_{16}, 3 megohms; R_8, R_9, 10,000 ohms; R_7, 5,000 ohms; R_5, R_9, 10 megohms; R_{11}, 20 megohms; R_{12}, 100,000 ohms wire wound precision; R_{13}, R_{14}, R_{15}, . . ., 0.5 megohm; R_{16}, 200,000 ohms; T_1, T_2, T_3, VR105; T_4, 920 phototube; T_5, 6C5; T_7, 6SJ7. $T_6$15—6L6. *F*, generator field; *M*, ammeter; *V*, separate voltage supply for screen grids of 6L6 tubes.

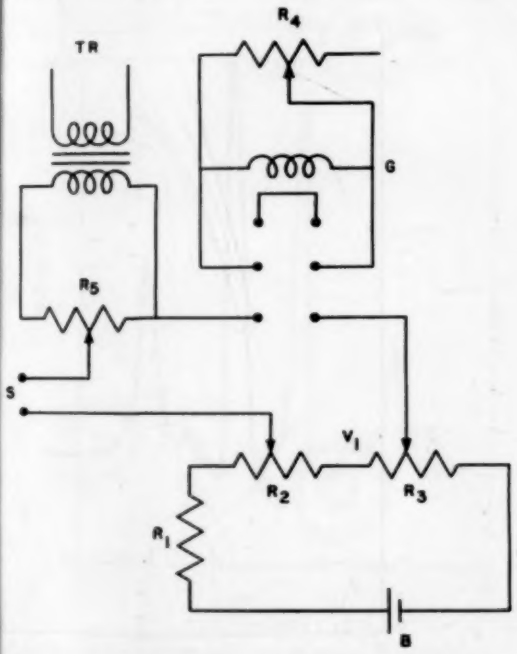

FIGURE 3.—*Diagram of circuit for the photocell galvanometer.*

R_1, 50,000 ohms; R_2, 70 ohms; R_3, R_4, 1,000 ohms; R_5, 10,000-ohm potentiometer; *TR*, transformer with 6.3 v secondary winding. *B*, 1.5 v dry cell. *G*, galvanometer coils. *S*, connection to 0.001-ohm shunt in series with generator armature and coils of spectrometer.

If the lens current tends to change, the balance in this circuit is upset so as to change the deflection of the galvanometer coil. The resulting change of illumination on the photocells changes the grid voltage of the 6SJ7 and hence the cathode voltage of the 6L6's, so as to change the generator field current to counteract the original change of the generator output. The lens current is in this way stabilized to about 0.1 percent. The presence of the low-voltage winding of a 6.3-v filament transformer is for the purpose of reducing fluctuations that might result from a tendency of the circuit to overcompensate.

Various settings of the lens current are obtained by selecting various values of V_1. The current is measured by passing it through an accurately calibrated shunt and measuring the voltage drop across it with a potentiometer.

In assembling the circuit, the photocell and its galvanometer are mounted separately on a wall bracket. This prevents any vibrations associated with operating the controls from upsetting the equilibrium of the galvanometer.

The 10 6L6's are mounted on a separate chassis. This chassis also contains a power pack supplying all voltages for the photocell circuit. A second chassis contains a power supply which provides screen voltage for the 6L6's. The rest of the circuit, including the meter, *M*, which indicates

the field current (the plate current of the 6L6's), the switch, S, for the 220-v d-c line, and the V_1 voltage supply, are mounted on a third chassis, the control chassis (which contains the three VR105 tubes, the 6SJ7 and 6C5, and their associated resistors).

When the circuit was first assembled the cathodes of the 6*L*6's (rather than the grids, as shown in fig. 2) were tied down to the point marked zero voltage (between the first and second VR105 tubes). Difficulty was encountered, however, because of the tendency of the circuit to go into high-frequency oscillation despite the presence of separate half-megohm resistors in the grid circuits of the 6L6's. When the points at which the grids and cathodes of the 6L6's are tied into the control circuit were interchanged (to give the circuit shown in fig. 2), this difficulty was eliminated.

In adjusting the circuit for operation, one proceeds as follows: V_1 is set at zero. The galvanometer position is adjusted to illuminate both photocells approximately equally. Switch S is then closed (the switch in the output circuit of the generator is kept open during this adjustment), and the grid of the 6SJ7 is adjusted by moving the tap on the 5,000-ohm potentiometer so that the plate current of the 6L6's has just begun to rise. Before closing the switch in the output circuit of the generator, the following test should be made. As V_1 is increased the light from the galvanometer lamp will sweep across the "increase" photocell (there being no opposing voltage from the 0.001-ohm shunt) until it leaves the photocell surfaces completely. As this takes place the plate current should pass through its maximum and then down to a value not far from 0. A low 6L6 plate current with zero illumination provides against a sudden large current rise should the galvanometer lamp burn out or its light leave the photocell surfaces for some other reason. The maximum 6L6 plate current should be adjusted in accordance with the arrangement of coil sections that is being used, by adjusting the 6L6 grid voltage through the tap on the 5,000-ohm potentiometer.

III. Radiations From 5.3 Yr Co^{60}

1. Calibration

For the initial work the source and detector were placed 100 cm apart, corresponding to a focal distance of 25 cm. The Geiger-Müller counter, which serves as a detector, has an opening 5 mm in diameter, and the mica window, which seals this opening, has a surface density of approximately 3.5 mg/cm².

The momentum of the focused electrons is expressible as $H\rho$, where ρ is the radius of the circular orbit these electrons would have in a uniform magnetic field, H. As the electron paths in the thin-lens spectrometer are quite complicated, no attempt is made to use the spectrometer as an absolute instrument. Instead, use is made of the fact that the lens coil contains no iron, so that the field, H, is proportional to the current, I. Hence, for a given source-detector arrangement, we may write $H\rho=kI$. k may be determined by studying electrons, whose momentum is well known. For this purpose the conversion electrons from a deposit of thorium B were used. Curves obtained with such a source are shown in figures 4 and 5.

In obtaining the data for figure 4, the four sections of the lens coil were connected in parallel. With such an arrangement of coils and a 100-cm

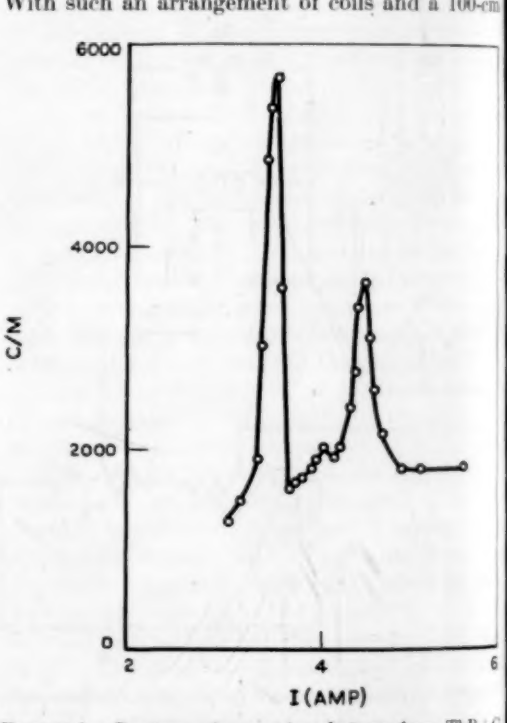

FIGURE 4.—*Spectrum of conversion electrons from* ThB+C *deposit used for calibration.*

All four coils in parallel. ThB No. 6; 4 coils parallel.

source-detector distance, electrons up to an energy of 2.5 Mev (with the present cooling provisions for the coil) can be studied. Higher energies are obtained by increasing the source-detector distance, but at a sacrifice in resolution.

In the spectrometer paper by Deutsch,[4] the $H\rho$ values for the two pronounced lines shown in figure 4 are given as 1,385 and 1,750. The first line has its peak at 3.48 amp, giving a k value ($H\rho$ per ampere) of 398. The second line has its peak at 4.38 amp. This corresponds to a coil constant of 399, and is a good check.

As an additional check some preliminary data have been obtained on the high-energy conversion line from the thorium source (from thorium C). The peak occurs at about 25.1 amp. If we use the $H\rho$ value of 10,080 given by Rutherford, Chadwick, and Ellis,[5] we again obtain a coil constant of 399. This serves to establish the linearity of the instrument throughout its range. This result is to be expected, as care was taken in construction to exclude any iron from the vicinity of the coil; the magnetic field and coil current are then related linearly throughout the range.

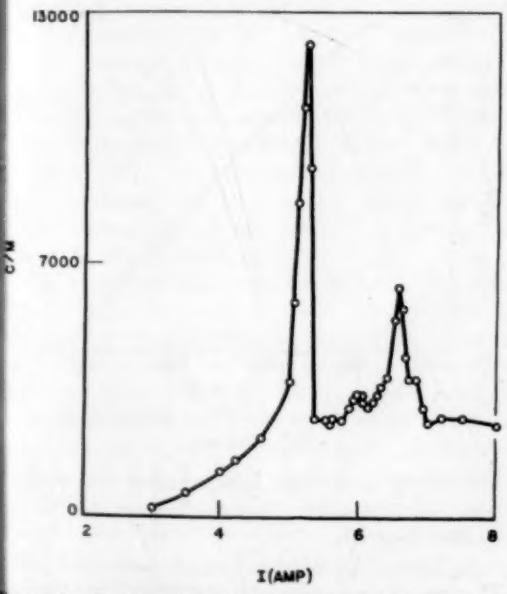

FIGURE 5.—*Spectrum of conversion electrons from* ThB+C *deposit used for calibration.*

Two outer coils only in parallel. ThB No. 6; 2 outer coils 11.

[4] See footnote 1.

[5] E. Rutherford, J. Chadwick, C. D. Ellis. Radiations from radioactive substances, p. 369 (Cambridge Univ. Press, London, 1930).

In figure 5 the thorium B spectrum is shown for another arrangement of the coil sections, namely, the two outer sections alone, in parallel. This arrangement is useful in the study of lower-energy radiations. With a 100-cm source-detector distance, electron energies up to 0.65 Mev can be studied with the present coil-cooling system. The two-section arrangement gives higher resolution than that of the four-section coil, or, for a given resolution, higher counting rates can be obtained when using the two-section arrangement.

In figure 5 the two strong thorium B lines occur at 5.20 and 6.55 amp. These give coil constants for this arrangement of 266 and 267 $H\rho$ per ampere, respectively.

2. Gamma Rays From 5.3 yr Co^{60}

The 5.3 yr Co^{60} isotope was found useful in determining some of the characteristics of the spectrometer. The supply of this isotope consisted of 50 mg of cobalt metal that had been irradiated for about 6 weeks in the pile at Clinton Laboratories.

For the spectrometer study a radiation source having a gamma-ray strength equivalent to about 5 millicuries of radium was prepared. The active material is placed in a brass capsule having a minimum wall thickness of 1 mm, so that all beta rays are absorbed. The radiator, from which the gamma rays eject photoelectrons, is placed as close as possible to the active material (in the present case about 1 mm). The radiator is placed in the same position as the thorium deposit used in the calibration work.

The photoelectrons from the radiator are focused by the spectrometer. The photoelectron peaks are superimposed upon a broad distribution of Compton electrons, ejected mostly from the brass capsule. The determination of the energy of the photoelectrons enables a determination of the gamma-ray energies. The radiations from 5.3 yr Co^{60} have been reported by Deutsch.[6] A curve showing data on the gamma rays from this isotope is given in figure 6.

For this curve all four coil sections, in parallel, were used. The radiator was a uranium foil of surface density 23 mg/cm^2. The curve shows L photoelectron peaks for the two gamma rays in

[6] M. Deutsch, L. G. Elliott, and A. Roberts, Phys. Rev. **68**, 193 (1945).

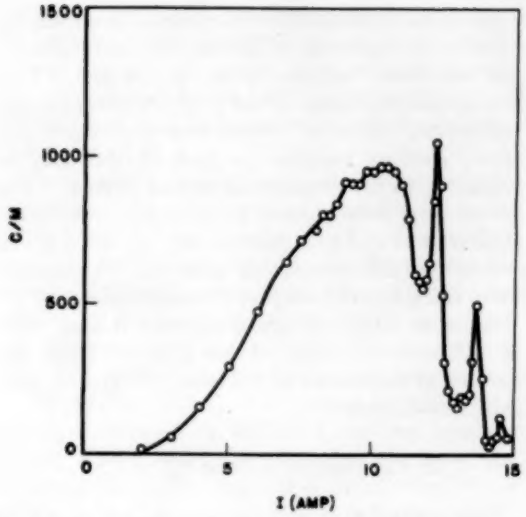

FIGURE 6.—*Spectrum showing the conversion spectrum for* Co^{60} *gamma rays in uranium radiator, of thickness 23* mg/cm^2.

Four coils in parallel. Co^{60} γ No. 2; V–23 radiator; 4 coils parallel.

addition to the pronounced K groups. The more complete structure in this curve over that of Deutsch is probably due to the use of uranium as radiator material instead of lead. The strength of the source made it possible to use a baffle arrangement giving fairly high resolution. The photoelectron peaks in figure 6 have a half-width ($\Delta\ p/p$, where p is the momentum) of about 0.02.

Knowing the binding energies of the K and L electrons in uranium, we can compute the energies of the two gamma rays from 5.3 yr Co^{60}. For the low-energy gamma ray, the K-electron peak is at 12.25 amp. Using the coil constant of 399 $H\rho$ per ampere, we get an $H\rho$ value for these photoelectrons of 4,890, or an energy of 1.045 Mev. Adding the K-binding energy of uranium, 0.115 Mev, there is obtained a gamma-ray energy of 1.16 Mev. The L-electron peak occurs at 13.125 amp, corresponding to an $H\rho$ of 5,240, and energy of 1.14 Mev. Adding the L-binding energy of uranium, 0.022 Mev, we again get a gamma-ray energy of 1.16 Mev. Similarly, the K and L electron groups from the high-energy gamma ray give us a value of 1.32 Mev for the gamma-ray energy. We estimate the values to be correct within 3 percent. The values given by Deutsch are 1.10 ± 0.003 Mev and 1.30 ± 0.03 Mev.

Figure 7 shows a graph of the beta-ray spectrum of 5.3 yr Co^{60}. The source was made by evaporating a solution of cobalt nitrate on an aluminum foil having a surface density of 2 mg/cm^2. The active material itself was also estimated to be about 2 mg/cm^2. As the beta rays are of fairly

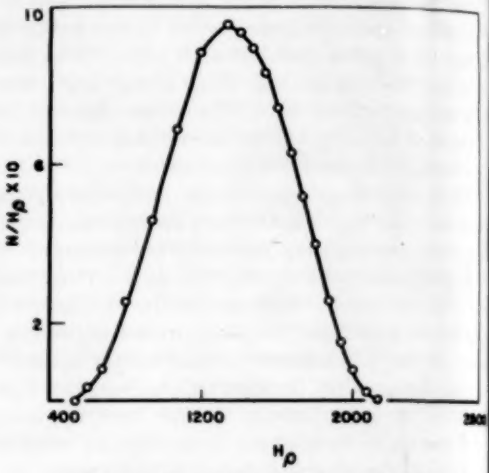

FIGURE 7.—*Beta-ray spectrum of* CO^{60}.

Co 6 No. 3.

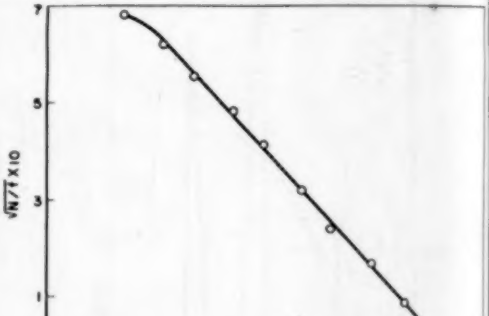

FIGURE 8.—*Fermi plot of* Co^{60} *beta-ray spectrum.*

Co^{60}; Fermi plot.

low energy, a thinner mica window (1.3 mg/cm^2 was used to cover the opening in the Geiger Müller counter.

A Fermi plot of the data is shown in figure 8. It gives an end point of 0.310 Mev. We estimate the uncertainty to be about 3 percent. Deutsch's value for the end-point energy is 0.308 ± 0.00 Mev.

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Preparation and Physical Properties of Several Aliphatic Hydrocarbons and Intermediates*

By Frank L. Howard, Thomas W. Mears, A. Fookson, Philip Pomerantz, and Donald B. Brooks

In the course of a continuing investigation of the knock ratings of aliphatic hydrocarbons, pure paraffins and olefins have been prepared in quantities sufficient for engine tests. This reports describes the methods of preparation and purification of three pentanes, four hexanes, three heptanes, four octanes, eight nonanes, seven decanes, four hexenes, five octenes, six nonenes, six decenes, and a number of alcohols, ketones, esters, and alkyl halides. Most of these compounds were highly purified. Physical constants measured include freezing point, boiling point, and its variation with pressure, refractive index, and density, and their variations with temperature.**

I. Introduction

In 1934 the Automotive Section of the National Bureau of Standards undertook an investigation of the impurities in the certified "isooctane" [1] used as a primary standard in the knock rating of fuels. In the course of this work, about a score of paraffin hydrocarbons were isolated, and their physical properties and knock ratings were determined [4].[2] The information obtained in this work indicated that some of the higher paraffin hydrocarbons should be decidedly superior to isooctane in knock rating.

The results of this work led in 1936, to a proposal to the National Advisory Committee for Aeronautics that a research project be initiated with the objective of preparing, in quantities sufficient for engine test, the paraffin hydrocarbons likely to be of interest as components of combat aviation fuel. This project was authorized to start July 1, 1937, under joint sponsorship of the National Advisory Committee for Aeronautics, the Army Air Corps (later, Army Air Forces), and the Navy Bureau of Aeronautics, and has been actively prosecuted since that time.

The results of portions of this investigation completed prior to 1940 have been described in earlier publications [4, 5, 6, 7]. The present paper describes the syntheses and physical properties of a number of aliphatic hydrocarbons, some of which have been covered in special restricted reports to the NACA Subcommittee on Aircraft Fuels and Lubricants.

As the objective of this work was the preparation of pure hydrocarbons for engine testing to determine knock rating, it was generally necessary to subordinate other considerations to this purpose. In many cases, it was therefore not possible to make detailed studies of the reactions, or to determine the properties of some of the new or little-known intermediates.

II. Apparatus

1. Reaction Vessels

Small-scale exploratory reactions were generally carried out in 5-liter glass flasks. In some cases, where an unusually low yield of final product was expected, 12-liter flasks were used.[3] For synthesis on a larger scale, two copper reactors were

*This paper has been issued by the National Advisory Committee for Aeronautics as Technical Note No. 1247 (1947).

**Several of the compounds investigated, 2,2,3,3-tetramethylpentane, 2,2,3,4-tetramethylpentane, 2,4-dimethyl-3-isopropylpentane, 2 pentamethylpentanes, and 3,3,4,4-tetramethylhexane, are believed to be new ones.

[1] The name "isooctane" is a widely accepted trivial name for 2,2,4-trimethylpentane. This nomenclature is used throughout this report.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] The use of 12-liter flasks was discontinued in 1944, and reactions of this size were then conducted in 14-liter brass double-walled vessels similar to the reaction vessels described later.

used initially. Each of these reactors had a capacity of 60 liters and was double-walled. Water at any desired temperature between 5° and 75° C could be circulated in the space between the walls to control the temperature of the reaction. The reactors were equipped with multiple paddle stirrers (60 to 200 rpm), reflux condensers (multiple copper tube), separatory funnels for addition of reactants, and draw-off valves for removal of products. These reactors were used until early in 1944, when two 50-gallon kettles (one glass-lined, one stainless steel) were put into service. The copper reactors were then used as distillation receivers in conjunction with the large kettles. The large kettles were standard commercial items and were installed so that any temperature between 5° and 150° C could be maintained in the jackets.

2. Hydrogenation Apparatus

Hydrogenation reactions were accomplished in high-pressure hydrogenators designed after those described by Adkins [1]. Three sizes were used, with capacities of 1, 3, and 20 liters. The catalyst used was a commercial nickel-on-kieselguhr preparation, which proved to be economical and efficient. No difficulty was encountered in hydrogenating any of the materials, provided they were halogen free. Most of the hydrogenation reactions took place at temperatures below 160° C, and pressures below 2,000 lb/in^2.

3. Stills

For convenience, the various stills used in this work are designated in the text by numbers. The salient features of these stills are given in table 1. Some of these columns are no longer in use, having been supplanted by others of later designs. Operations formerly performed in columns 1 and 2 were later carried out in 19 and 20, and columns 8 and 9 were replaced by 17 and 18. Column 10 was abandoned in 1942, when column 11 was put into operation. Columns 3 to 7 were replaced by columns 21 to 27 late in 1945.

Still 1.—This still has been previously described [7]. The reflux rate was approximately 1,500 ml/hr in most cases, the take-off rate being governed by the composition of the charge and the purity desired in the product. Samples of 78 ml each were removed automatically at predetermined intervals of ½ to 24 hr. The efficiency is approximately 90 to 95 theoretical plates, and the holdup is 260 ml.

TABLE 1.—*Distillation columns*

Still No.	Type	Size	Packing	Pot capacity
		cms		ml
1	Total reflux intermittent take-off.	600 by 4.0	3/16-in. Pyrex helices	5,000
2 [a]				5,000
3	Total reflux variable take-off.	150 by 2.0	3/16-in. glass helices	200 to 5,000
4	do	150 by 2.2	3/32-in. stainless steel helices from 0.010-in. wire.	200 to 5,000
5	do	150 by 2.2	do	200 to 5,000
6	do	150 by 2.2	3/16-in. glass helices	200 to 5,000
7	do	125 by 2.2	do	200 to 5,000
8	do	70 by 1.1	1/16-in. Nichrome helices from 0.010-in. wire.	100 to 500
9	do	40 by 1.0	3/64 in. stainless steel helices from 0.0065-in. wire.	250
10	do	243 by 5.1	Sash chain	40,000
11	do	600 by 5.1	35-in. 1/2-in. carbon raschig rings, then 200 in. 3/32-in. stainless steel helices from 0.010-in. wire.	75,000
12 & 13	do	1,600 by 10.2	3/8-in. porcelain raschig rings.	227,000
14	do	1,600 by 5.1	19.7 in. 3/8-in. porcelain raschig rings, followed by 600-in. 3/32-in. stainless steel helices from 0.010-in. wire.	227,000
16	do	1,600 by 2.7	do	113,000
17	Podbielniak hypercal.	127 by 0.8	Heli-grid	250 to 5,000
18	do	127 by 2.5	do	250 to 5,000
19 & 20	do	250 by 2.5	do	250 to 5,000
21	Dephlegmator controlled take-off.	120 by 3.5	3/16-in. glass helices	22,000
22 to 25	Total reflux variable take-off.	183 by 2.5	3/32-in. stainless steel helices from 0.010-in. wire.	500 to 5,000
26 & 27	do	183 by 2.5	3/16-in. glass helices	500 to 5,000

[a] See text.

Still 2.—The column of this still consists of 150 actual plates, following the design by J. H. Bruun [8]. The volume of each fraction removed was 65 ml. Reflux rate was about 800 ml/hr. This still has also been described [7]. The mechanisms of operation and sample removal are the same as for still 1.

In both stills (1 and 2) the head temperature was followed during the day by means of a platinum resistance thermometer, and the timing operations were scheduled so that samples were

removed when this temperature (corrected to 760 mm Hg) became reasonably constant (generally to within a change of less than 0.005 deg C/hr).

Stills 3 to 9.—Small stills patterned after those described by Whitmore and Lux [40] were used to remove ether from reaction mixtures, for purification of intermediates, for preliminary purification of final products, and for fractionation of small charges. These stills are designated as 3 to 9 in table 1.

Still 10.—Prior to the construction of other large-capacity stills, still 10 was used for preliminary fractionation of commercial synthetic crudes. The pot was part of a domestic hot-water tank, the column a length of 2-in. pipe. The take-off was governed by a ⅛-in. needle valve.

Still 11.—In order to have a higher-capacity, higher-efficiency still than No. 10, still 11 was constructed. The entire still is made of monel metal. The reflux rate is about 4 liters/hr, as measured by gain in temperature of the condenser water. The take-off rate is governed by a commercial ¼-in. solenoid valve operated by an automatic-timing device. The efficiency of the still is about 65 theoretical plates under operating conditions (3.5 to 4.5 liters/hr reflux). Safety devices include overflow tanks for the salvaging of material distilled through the condenser if the water is accidently cut off, a product-overflow tank for retaining material that may be delivered because of faulty operation of the solenoid valve, and a pot-temperature limit control. All openings to the still are vented to the outside of the building.

Stills 12 to 16.—These columns were constructed for analysis of commercial crudes, purification of large quantities of material, and isolation of hydrocarbons from commercial mixtures. These were put into operation in 1943, and later (1945) column 11 was lengthened by 4 ft and added to the group. The take-off on all these stills is governed by a timer and small solenoid valves. Condensers in the larger columns are of the multiple cold-finger type. The columns are heated by resistance wire controlled by variable transformers. Temperatures are measured by copper-constantan thermocouples.

Safety devices include overflow tanks, automatic pot-temperature limit control, forced ventilation, automatic carbon dioxide fire control (controlled by thermal plugs), and automatic warning if the atmosphere approaches a combustible mixture.

The pots of stills 12 to 16 are made of mild steel. The columns of stills 12 and 13 are made of galvanized pipe; the columns of stills 14 and 15 are made of stainless steel. The condensers are of copper, brass, or monel metal.

Credit is due M. R. Fenske [16], of the Petroleum Refining Laboratory at Pennsylvania State College, for advice on the design and operation of stills 11 to 16.

III. Methods and Technic

1. Preparation of Grignard Reagents

The preparation of Grignard reagents in large quantities (up to 330 moles) has been found to be subject to the same limitations as the preparation of small amounts, except that the yields, in general, are slightly larger. The methods used in typical runs of representative members of the aliphatic series are given below, and are not repeated in the discussion of the various syntheses. Decomposition of reaction complexes formed by the action of Grignard reagents on various compounds followed the classical methods and need not be repeated.

Methylmagnesium bromide.—To the reactor was added 100 gram atoms (2.43 kg) of magnesium turnings and enough ether to cover the magnesium. A small amount of methyl bromide was added. If reaction did not start immediately, a little methyl iodide (or previously prepared Grignard reagent) was added. After reaction had been initiated, the stirrer was started, and methyl bromide from a cylinder supported from a steelyard was allowed to flow through a coil of copper tubing surrounded by a dry-ice bath where it condensed and dropped into the reaction mixture. Flow was regulated by a small needle valve. After the reaction was well started, cooling water was admitted to the jacket, and methyl bromide was added as fast as it would react. During the addition of methyl bromide, ether was added in 2-liter portions until the total ether added was 20 liters (200 ml/gram atom of magnesium). The amount of methyl bromide added was determined by the loss of weight of the cylinder, and it was found that practically no methyl bromide was lost during the operation. After addition of methyl bromide was complete, the reaction mixture was warmed for 2 to 3 hr. If the mixture contained sludge or pieces of unreacted magnesium,

it was allowed to stand until the sludge had settled, then the clear solution was siphoned off. The sludge was then washed with dry ether, allowed to settle, and the siphoning procedure repeated. If the amount of sludge was small, this latter operation was advantageously carried out in a separatory funnel, where the sludge could be drawn off easily.

The yields varied from 88 to 95 percent, based on magnesium as determined by titration. Similar yields were realized when ethylmagnesium chloride was prepared, but in this case slower addition of halide was necessary in order to avoid the formation of appreciable amounts of sludge.

Isopropylmagnesium chloride—Magnesium turnings (1.5 kg, 63 gram atoms) and 5 liters of ether were placed in the reactor, and reaction was started by the addition of a small amount of isopropyl chloride. After the reaction was initiated, the stirrer was started and 1 liter of isopropyl chloride in 2 liters of ether was added slowly. After this first charge of chloride was complete, 5 liters of ether and the rest of the magnesium (1.5 kg, 63 gram atoms) were added, and cooling water was circulated through the jacket. Then the rest of the chloride and ether was added in the ratio of 1 liter of chloride to 2.0 to 2.5 liters of ether, until a total of 125 moles of chloride and 37.5 liters of ether had been used. This addition was carried out as fast as possible, still keeping the reflux from the condenser dropwise and not in a steady stream. About 35 hrs were required for a 125-mole run. After removal of the clear solution from the sludge, the yield, calculated from titration data, amounted to 90 to 93 percent of the theoretical quantity.

t-Butylmagnesium chloride.—This preparation was carried out in essentially the same manner described above for the preparation of isopropylmagnesium chloride, except that the addition of chloride was necessarily slower, in order to retard formation of hexamethylethane, isobutylene, and diisobutylene. A 70-mole run required approximately 35 hr. The latter half of the chloride added was more dilute than the first half [33], and the rate of addition was slowed up progressively as the reaction neared completion. The jacket of the reactor was not cooled as much in this preparation as with the less highly branched halides. The tendency of *t*-butyl chloride to form sludge is much greater than that of the simpler halides, although many runs were made in which practically no sludge was observed. The yields varied from 80 to 92 percent.

2. Determination of Physical Properties

From the plots of refractive indices, boiling points, or freezing points of fractions with respect to volume of distillate, those fractions containing the "best" material were selected and used for the determination of physical constants.

The methods used for the determination of physical constants have been described previously [6]. The freezing-point apparatus was modified in December 1944, so that additional control of the rate of cooling could be obtained. This was done by installing a pumping system on the evacuated chamber surrounding the sample, so that the rate of cooling could be governed by the pressure in the evacuated chamber. This modification of the equipment has been adequately described by Mair [24].

The freezing-point data on 2,2,5,5-tetramethylhexane are considered representative and are illustrated in figure 2. Boiling-point data on samples of four compounds are shown in figure 1. These figures are presented as typical examples of actual measured physical properties.

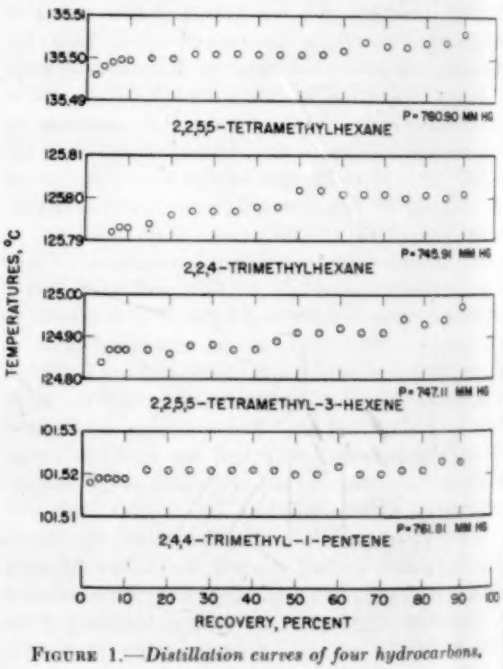

FIGURE 1.—*Distillation curves of four hydrocarbons.*

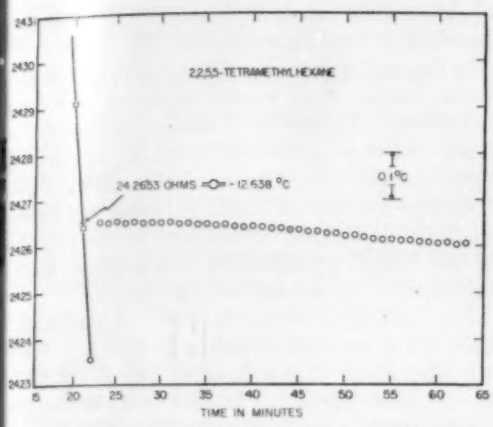

FIGURE 2.—*Freezing curve of 2,2,5,5-tetramethylhexane.*

Refractive indices were measured on an Abbe type (Valentine) refractometer until 1943, when a Bausch & Lomb "precision oil" refractometer (also Abbe type) was put into use. Table 6 lists the measured physical properties of the compounds herein.

A rough estimate of the purity of the individual compounds may be made from the "ΔT:20 to 80 percent" listed beside the boiling-point data in table 6. This figure is the number of degrees difference between the temperature at which 20 percent of the material had distilled and the temperature at which 80 percent had distilled. The presence of peroxides in the olefin samples tend to make this value extraordinarily large. The ultimate measure of purity is made by a consideration of the freezing point.

IV. Preparation of Materials

1. n-Pentane

One gallon of *n*-pentane, which was obtained by purchase, was fractionated in still 1. From this distillation there was obtained 1,792 ml of material, the fractions of which had a refractive index (n_D^{20}) of 1.3574 to 1.3575. A "best" sample was selected for determination of physical constants.

2. 2-Methylbutane (Isopentane)

One gallon of commercial isopentane was fractionated in still 1. There was obtained 2,200 ml of material, n_D^{20}=1.3535 to 1.3536, which was collected while the head temperature of the column was 27.87° to 27.88° C. Later, a total of 47 liters of high-purity material was prepared from the same source by fractionation in still 11.

3. 2,2-Dimethylpropane (Neopentane)

In 1933 Whitmore and Fleming [36] described the preparation of neopentane by reaction between methylmagnesium chloride and *t*-butyl chloride in toluene at 45° to 50° C. Yields of 42 to 50 percent were reported. In the present work, a method is described whereby somewhat larger yields of purer product were obtained.

In this work, neopentane was prepared by action of dimethyl zinc on *t*-butyl chloride in toluene at 5° C. The advantage of causing reaction at this temperature, rather than the often used higher temperature (35° to 50° C) for reactions of this type has been previously demonstrated [19]. Dimethyl zinc was prepared in the manner previously reported [19]. However, certain improvements in the technic of handling this material have been made. For these improvements credit is due N. L. Drake and A. Sadle, of the University of Maryland [12].

A 5 liter, single-neck flask, which was used for dimethyl zinc preparation, was placed in an oil bath, and fitted with a 400-mm reflux condenser. To the top of the condenser was attached a bridge of 10-mm glass tubing, which led to the top of a similar reflux condenser attached to a 5-liter, three-neck flask. This latter flask, into which dimethyl zinc was distilled, was situated in a cold-water bath and was provided with a separatory funnel (500 ml) and a stirrer. A side arm on the bridge provided for the introduction of inert gas (carbon dioxide).

The zinc-copper couple from 960 g of zinc dust and 120 g of cupric oxide was placed in the one-neck flask, and 1,100 g (7.75 moles) of methyl iodide added. The temperature of the oil bath was raised to about 45° C, and a slow stream of carbon dioxide was passed in the side arm of the bridge and out through the separatory funnel, into a venting tube made of 25-mm glass tubing. Reaction between methyl iodide and the couple was complete after 10 hr, provided that the couple was sufficiently active. When reaction had ceased, as shown by the cessation of reflux, the carbon dioxide flow was stopped, 500 ml of toluene was added to the three-neck flask, and the top of the separatory funnel was fitted with a

T-tube. The reflux condenser on the one-neck flask was heated with steam, and the temperature of the oil bath was gradually raised over a period of 2 hr to about 180° C. This caused the methylzinc iodide in the flask to decompose into dimethyl zinc (and zinc iodide). The dimethyl zinc distilled across the bridge into the toluene in the three-neck flask. Carbon dioxide was allowed to flow through the top of the T-tube while distillation of dimethyl zinc was in progress.

After distillation of dimethyl zinc was complete, the single-neck flask was allowed to cool and the side arm on the bridge connected to a gas-purification train comprising, in the order named, a wash bottle containing water, two bottles containing 85 percent sulfuric acid, an empty bottle, one containing 40 percent potassium hydroxide, a calcium chloride drying tower, and a 100- by 1.5-cm tube filled with silica gel. After passing through this train, the gas was led into a condensing system comprising a copper-coil condenser at −10° C, a receiver at −78° C, and finally a trap at −78° C.

The flask containing toluene and dimethyl zinc was cooled to 5° C, and 525 ml (about 4.8 moles) of *t*-butyl chloride in 750 ml of dry toluene was added during 5 hr. During the addition of chloride, methane was evolved by the reaction. After the addition of chloride was complete, the reaction mixture was allowed to stand 15 hr. Then the bath temperature was raised gradually to 50° C, during which time more gas was given off, which was not affected by the sulfuric acid and which did not condense in the −78° C trap.

Water was then added to the reaction mixture through the separatory funnel. It was necessary to exercise considerable care in this operation as a violent evolution of neopentane took place at this point. This gas was condensed in the −10°C condenser and solidified in the receiver. There was no discoloration of the sulfuric acid. After about 200 ml of water had been added, and the evolution of gas had subsided, the apparatus was swept out with nitrogen.

The resulting neopentane was transferred to a glass tube and sealed. The yield amounted to 164.5 g, which is 59 percent of that theoretically possible, based on one-half the amount of methyl iodide used. (Two moles of methyl iodide give 1 mole of dimethyl zinc.)

The residue from the distillation of dimethyl zinc, which contained zinc iodide, was used to prepare additional methyl iodide by the method described in Organic Syntheses [28].

In assembling the apparatus, corks coated with shellac, rather than rubber stoppers, were used exclusively. In one preliminary experiment, in which rubber stoppers were used, the product was contaminated with a material that had the odor of methyl mercaptan. Where rubber tubing was necessary in making connections to the side arm on the bridge, arrangement was made so that a minimum of rubber surface was exposed.

The yield reported on the first run was verified later, when nine additional runs of this preparation were made, in which an average yield of 65.6 percent was obtained. In two of these runs, the couple was less active than in the other preparations, and the product was contaminated with methyl iodide. The presence of methyl iodide was characterized by a pink color that developed in the product after a few days. The yield obtained in one run was low because a stoppage developed in the purification train, and some material was lost through a loosened connection.

Freezing-point measurements made on the material from three experiments gave the values −16.61°, −16.61°, and −16.60° C, respectively. These values may be compared with the value −16.63° ±0.10° C calculated for the freezing point of 100-percent pure neopentane by Aston and Messerly [2].

4. 3-Methylpentane

From 75.2 moles of ethylmagnesium chloride and 37 moles of ethyl acetate there was prepared 3,660 ml of 3-methyl-3-pantanol, which was purified by distillation in column 7 (bp 120° to 124° C at 760 mm). Dehydration of this carbinol by refluxing with 0.2 percent β-naphthalene sulfonic acid yielded a mixture of alkenes that boiled at 65° to 71° C at 758 mm. This dehydration would be expected to yield chiefly 3-methyl-2-pentene, with a smaller amount of 2-ethyl-1-butene. No attempt was made to separate the two olefins as both compounds yield the same alkane when hydrogenated. Hydrogenation of this mixture gave crude alkane, which was filtered through silica gel and distilled in column 4 to yield 1,980 ml of material that boiled at 64.5° to 65.5° C (uncorrected). Redistillation in column 1 gave 1,420 ml of hydrocarbon made up of fractions removed while the head temperature was

63.319° to 63.322° C (761.1 mm Hg) and for which n_D^{20}=1.3764 to 1.3765.

5. 2,2-Dimethylbutane (Neohexane)

The synthesis of neohexane has been reported previously from this laboratory [7]. Since then, "commercial" neohexane has become available. Several charges of this material were fractionated in stills 1 and 2. From each run, only the latter half of the distillate consisted of material having the properties of neohexane. The forerun contained an impurity of higher refractive index and had a slightly lower boiling point. No extensive investigation was made of this forerun, but the most likely impurity was cyclopentane. This fact was later substantiated by the manufacturer.

A total of 38 liters of purified neohexane was prepared by fractionation of 75 liters of the commercial crude mixture in still 11.

6. 2-Methylpentane

About 75 liters of commercial crude neohexane was fractionated to prepare 38 liters of 2,2-dimethylbutane. From the distillations of this material there was obtained 3,320 ml of residue, which was fractionated in column 2 into 46 fractions:

Fraction	Boiling range (° C)	Volume (ml)	Refractive index (n_D^{20})
to 22	58.8 to 60.2	1,500	1.3748 to 1.3717
3 to 44	60.2 to 60.4	1,500	1.3715 to 1.3717
5 to 46	60.4	140	1.3717 to 1.3744

Fractions 35 to 37 were combined, filtered through silica gel, and used in the determinations of physical properties of 2-methylpentane.

7. Investigation of "Butene Alkylate"

Seventy-five liters of "butene alkylate" (Humble Oil Co.) was fractionated in still 10. The head temperature was measured by means of a recording thermometer of the gas-expansion type. The reflux ratio was maintained at about 100 to 1. Fractions of not more than 3.87 liters each were collected, the volume of the fraction depending on the time-temperature curve. After the measurement of refractive indices, like fractions from different runs were combined and refractionated in still 2. Fractionation of the lowest boiling portion from still 10 was carried out first, then the second lowest boiling portion was added to the residue and fractionated, and so on. The refractive index of each fraction was measured, and a plot of refractive index versus fraction number was made. Samples represented by single plateaus were combined and redistilled in column 1 or 2. Several hydrocarbons were isolated thereby and are listed in table 2.

TABLE 2.—*Hydrocarbons isolated from "Butene Alkylate"*

Hydrocarbon	Boiling point at 760 mm Hg (Cottrell)	Refractive index (n_D^{20})	Volume isolated	Volume of total butene alkylate [a]
	°C		ml	Percent
Isopentane	27.9	1.3531 to 1.3533	728	0.97
2, 3-Dimethylbutane	57.9	1.3749 to 1.3752	2,213	2.97
2-Methylpentane	60.2	1.3714 to 1.3716	224	0.30
3-Methylpentane	63.2	1.3761 to 1.3763	224	.30
2, 4-Dimethylpentane	80.5	1.3815 to 1.3820	2,610	3.44
2, 3-Dimethylpentane	89.9	1.3912 to 1.3920	1,034	1.37
2, 2, 4-Trimethylpentane	99.3	1.3912 to 1.3915	11,727	15.48

[a] The data in this column represent the amount isolated having the properties shown. It does not constitute an exact analysis of the crude.

(a) 2,3-Dimethylbutane

The 2,3-dimethylbutane from "butene alkylate", (2,213 ml) was added to 1,255 ml of 2,3-dimethylbutane of approximately the same purity. (This sample of hydrocarbon was furnished by the Standard Oil Co. of Indiana, through the courtesy of D. P. Barnard and R. F. Marschner). The combined material was washed with sulfuric acid, water, sodium carbonate solution, and again with water. After it was dried and filtered through silica gel, it was fractionated in still 2, and gave 2,300 ml of material, for which n_D^{20}=1.3748 to 1.3749.

(b) 2,4-Dimethylpentane

The 2,4-dimethylpentane from "butene alkylate" (2,610 ml) was refractionated in still 2. The fractions for which n_D^{20}=1.3816 to 1.3817 were reserved as the best portion and amounted to 985 ml.

8. 2,3-Dimethylpentane From "Isooctane"

Seventy-five liters of "isooctane" (Phillips Petroleum Co.) was fractionated in still 10 in the manner described in section IV–7. Fractions that distilled between 85° and 95° C (n_D^{20}=1.3886 to 1.3914) were combined (28,051 ml) and refractionated in still 11. From this distillation there was obtained 7,165 ml of hydrocarbon that boiled at 89.7° to

90.0° C (n_D^{20}=1.3918 to 1.3921), which was refractionated in still 2. The purified 2,3-dimethylpentane thereby obtained amounted to 4,790 ml after filtration through silica gel. The refractive-index range (n_D^{20}) of various fractions was 1.3919_1 to 1.3919_8.

9. 2,2,3-Trimethylbutane (Triptane)

The synthesis of triptane involved the following two reactions: (a) The preparation of 2-chloro-2,3-dimethylbutane, and (b) the reaction of this chloride with dimethyl zinc.

(a) 2-Chloro-2,3-dimethylbutane

The apparatus used was similar to that described by Howard [19] for the preparation of 4-chloro-2,4,4-trimethylpentane. It was modified so that rubber stoppers were replaced with ground-glass connections. The alkene used was a mixture of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene, which was formed by dehydration of pinacolyl alcohol (3,3-dimethyl-2-butanol) [7]. The original alkene mixture contained a small amount of 3,3-dimethyl-1-butene in addition to the above-named hexenes, but this hydrocarbon was removed for use in another synthesis.

In 2 hr, 1,500 ml of the alkene mixture, along with excess hydrogen chloride, was passed through two chambers kept in a bath at −78° C. Occasionally it was necessary to remove the baths in order to allow the solidified chloride to melt and pass on through the apparatus. The product was washed with water, with 5 percent sodium bicarbonate solution, again with water, and dried with two successive portions of fresh anhydrous potassium carbonate. Distillation of the resulting material in column 3 gave, after a forerun of unchanged alkene, 675 g of 2-chloro-2,3-dimethylbutane (bp 69° to 70° C at 190 mm Hg).

(b) Synthesis of Triptane

In an apparatus like that which was used in the preparation of neopentane (section IV–3), dimethyl zinc was prepared from 1,100 g (7.75 moles) of methyl iodide and distilled into a 5-liter flask containing 500 ml of toluene. The flask was surrounded by ice, and the chloride (600 g, 5 moles) in 1,000 ml of toluene was added during 4 hr. The mixture was allowed to stand for 16 hr, and was then treated with water and with dilute hydrochloric acid. The reaction product (2,060 ml) was fractionated in column 5 to give a small amount of methyl iodide, some olefinic material presumably consisting of dimethylbutenes formed by dehydrochlorination of alkyl chloride, and 297 ml of crude triptane boiling at 78° to 83° C, with n_D^{20}=1.3932. Two passages through silica gel give a product of the following properties, compared with those of high-purity material:

	This preparation	High-purity material [7]
Refractive index (n_D^{20})	1.3897	1.3897
Density (d_4^{20})	0.6896	0.6900
Freezing point (°C)	−26.1	−25.09
Boiling point (°C)	81.0 (Cottrell)	80.879

The yield of crude triptane amounted to 51 percent of the theoretical.

In subsequent experiments it was found that a large excess of alkyl chloride offered no advantage, a 2 to 3 percent excess giving a comparable yield. The excess chloride was found to be easily removed by boiling the crude mixture with a 5-percent solution of potassium hydroxide in alcohol.

In each of several experiments, the yield amounted to 46 to 52 percent of crude triptane. The time allowed for addition of chloride was varied from 3 to 8 hr and the temperature of reaction from 0° to 30° C without any appreciable change in yield. In one experiment, in which "isooctane" (2,2,4-trimethylpentane) was used as a solvent, the yield was 48 percent.

Under the conditions of hydrochlorination, 2,3-dimethyl-1-butene was found to add hydrogen chloride more easily than 2,3-dimethyl-2-butene. The unreacted alkene that was recovered when a mixture of the two was hydrochlorinated was found to be practically pure 2,3-dimethyl-2-butene.

Very slight decomposition of 2-chloro-2,3-dimethylbutane takes place when it is boiled at atmospheric pressure.

10. 2-Methyl-3-ethylpentane

This octane was prepared by hydrogenation of the olefins which resulted from the dehydration of 2-methyl-3-ethyl-3-pentanol. The carbinol was prepared by the action of ethylmagnesium chloride on isobutyl isobutyrate.

To a solution containing 90 moles of ethylmagnesium chloride in 20 liters of ether was added 6,335 g (44 moles) of isobutyl isobutyrate in 10.5 liters of ether. The product was dried with sodium carbonate and distilled in column 6. There was obtained 5,680 ml of 2-methyl-3-ethyl-3-pentanol (55° to 57°C at 48 mm Hg). Dehydration was effected by refluxing the carbinol with 0.2 percent by weight of β-naphthalene sulfonic acid, which gave 5,235 ml of crude alkene mixture, boiling at 114° to 119°C. As dehydration of 2-methyl-3-ethyl-3-pentanol should yield two alkenes, namely, 2-methyl-3-ethyl-2-pentene (bp ca 117°C) and 4-methyl-3-ethyl-2-pentene (bp ca 116°C), both of which yield the same alkane on hydrogenation, no attempt was made to separate the two. The alkene mixture was dried with calcium chloride and distilled from sodium. A portion of the distillate (4,721 ml) was hydrogenated to the alkane, which, after two distillations from sodium and filtration through silica gel, amounted to 4,050 ml. The compound was finally fractionated in still 1, yielding 3,300 ml of material, which had a refractive index constant within 0.0001.

11. 2,3,3-Trimethylpentane

This hydrocarbon resulted from the reaction between isopropylmagnesium chloride and *t*-amyl chloride.

To 90.5 moles of isopropylmagnesium chloride in 30.9 liters of ether solution was added 9,600 g (90 moles) of *t*-amyl chloride during a period of about 12 hr. Stirring was continued until separation of solid material prevented adequate mixing. Then the reaction mixture was allowed to stand 2 to 3 weeks at 15° to 20°C until no more Grignard reagent was present. The product was treated with ice and dilute hydrochloric acid and the resulting organic material distilled in column 3. After a forerun of ether, isoamylene, and *t*-amyl chloride there was obtained 4,400 ml of crude 2,3,3-trimethylpentane (31% yield), which boiled 112° to 115°C. When refractionated in column 1, the crude paraffin gave 3,600 ml of fractions for which n_D^{20}=1.4074 to 1.4075. Redistillation of accumulated foreruns from several batches gave an additional quantity of pure material. From several runs a total of 39 liters of pure 2,3,3-trimethylpentane was prepared.

Early experiments on this preparation were made in which a large excess of Grignard reagent was assumed to be desirable, but it was found that the yield of product was actually decreased by an excess of Grignard reagent. For example, in one run in which 72 moles of isopropylmagnesium chloride was allowed to react with 57 moles of *t*-amyl chloride, the yield of 2,3,3-trimethylpentane was only 21 percent. Credit is due Doctors Calingaert, Beatty, and Soroos [9] for the discovery of this improvement in technic, which they made in connection with a similar reaction.

12. 2,2,3-Trimethylpentane and 2,3,4-Trimethylpentane

There was prepared, by fractionation of several cuts of alkylate mixtures, 38.6 liters of 2,2,3-trimethylpentane and 37.9 liters of 2,3,4-trimethylpentane. The source materials were selected fractions of Shell Oil Co. "hot acid octane" (208 liters), Phillips Petroleum Co. "isooctane" (38 liters), Universal Oil Products Co. "isooctane" (45 liters), and previously prepared synthetic material (0.6 liter) [6]. The unresolved alkylates and residues were roughly fractionated in stills 10 and 11 into concentrates rich in 2,2,3-trimethylpentane and 2,3,4-trimethylpentane. These concentrates were redistilled in column 11. Most of the material was obtained by these distillations. Foreruns, intermediates, and afterruns were again fractionated in stills 1 and 2. From a total of 47 distillations there was obtained 38,610 ml (at 25° C) of 2,2,3-trimethylpentane (n_D^{20}=1.4026 to 1.4029) and 37,955 ml (at 25° C) of 2,3,4-trimethylpentane (n_D^{20}=1.4041 to 1.4045). Physical constants of the two compounds were measured and agreed well with those measured on the pure materials, as reported previously [6, 7].

13. 2,2,5-Trimethylhexane

The presence of 2,2,5-trimethylhexane in "isooctane residue" was reported by Brooks, Cleaton, and Carter in 1937 [4]. By distillation of 76 liters of this material [4] in still 10, a concentrate rich in this nonane was obtained. This concentrate (4,525 ml, bp 123° to 125° C, n_D^{20}=1.399 to 1.400) was refractionated in still 1. There was obtained 2,005 ml of 2,2,5-trimethylhexane, with a refractive-index range of 1.3995–1.3996.

[4] Supplied by the Rohm & Haas Co.

14. 2,3,5-Trimethylhexane

This nonane was prepared by hydrogenating 2,3,5-trimethyl-2-hexene, which resulted from the reaction of isopropylmagnesium chloride on 1-chloro-2,3-dimethyl-2-butene. There was also formed a small amount of 2,3,3,4-tetramethyl-1-pentene in this reaction.

(a) 2,3-Dimethyl-1,3-butadiene

Pinacol hydrate, prepared by the method of Brooks, Howard, and Crafton [7] was dehydrated to anhydrous pinacol by distillation in columns 4 to 7. These distillations were carried out at atmospheric pressure until the head temperature reached 122° C, when the pressure was reduced to 80 mm Hg. At this pressure the anhydrous pinacol distilled at 111° to 114° C.

In order to determine the optimum conditions for conversion of the glycol to 2,3-dimethyl-1,3-butadiene, a series of test runs were made. The results are shown in table 3. In these experiments the pinacol was refluxed with the catalyst under columns 5 or 7. The product of each run was washed, dried, and distilled in column 6 for analysis. From the results of these experiments it was concluded that 48 percent hydrobromic acid was the best catalyst of those tried for this dehydration. By dehydrating several batches of pinacol (2.5 to 3.0 kg per batch), 17.4 liters of 2,3-dimethyl-1,3-butadiene was prepared, which boiled at 68.5° to 71.5° C at 758 mm.

TABLE 3.—*Dehydration of pinacol to 2,3-dimethylbutadiene-1,3 and pinacolone (3,3-dimethyl-2-butanone)*

Run	Pinacol taken	Catalyst	Yield of—	
			Dimethyl butadiene	Pinacolone
	g		*Percent*	*Percent*
1	453	1.5 g of 48-percent hydrobromic acid.	45	19
2	500	5.0 g of β-naphthalene sulfonic acid.	36	34
3	500	5.0 g of *p*-toluene sulfonic acid	40	31
4	500	7.0 g of aniline hydrobromide	18	15

(b) 1-Chloro-2,3-dimethyl-2-butene

The addition of hydrogen chloride to 2,3-dimethyl-1,3-butadiene was accomplished in the apparatus described by Howard [19]. The reaction chambers were kept at −30° C, and dry hydrogen chloride and alkadiene was added simultaneously. The daily output of the apparatus was 1.0 to 1.5 liters of chloride. The product was freed of dissolved hydrogen chloride by aeration with carbon dioxide and stored over sodium carbonate. Distillation analysis showed that the reaction was practically quantitative. The product used for further synthesis boiled at 32° C at 45 mm Hg.

(c) 2,3,5-Trimethyl-2-hexane

To an ether solution of 62 moles of isopropylmagnesium chloride was added 7.32 kg of 1-chloro-2,3-dimethyl-2-butene. The reaction mixture became very viscous, and it was necessary to add more ether at intervals. The reaction was worked up after 4 days, and the organic material was dried, the ether removed, and the crude residue distilled through column 3 (bp 70° to 71° C at 90 mm, $n_D^{20}=1.4299$). Although there was no appreciable forerun, a large amount of high-boiling material (175° to 200° C) was present. This material was not identified, but is presumed to be polymers (dimers and trimers) of the alkadiene, formed under the influence of the Grignard reagent.

The crude 2,3,5-trimethyl-2-hexene contained a considerable quantity of chloride, the greater part of which was removed by boiling with alcoholic potassium hydroxide. Hydrogenation of the crude alkene gave 2,3,5-trimethylhexane, which was filtered through silica gel and distilled in column 3. From 2,500 ml of material there was obtained 900 ml that boiled at 131.9° C ($n_D^{20}=$ 1.4060 to 1.4061) and 50 ml of a hydrocarbon t boiled at 141.9° C ($n_D^{20}=1.4218$). The latter was identified as 2,3,3,4-tetramethylpentane by comparison with a sample prepared in another manner. A residue of about 1 liter that boiled above 165° C resulted from this distillation. This residue was probably formed by the action of potassium hydroxide or hydrogenation catalyst on the unsaturated halide which was in the crude olefin. Obviously, most of the Grignard reagent was dissipated in side reactions rather than by coupling with the chloride in the expected manner. This tendency could possibly have been decreased by carrying out the reaction in a more dilute solution.

This preparation was made in 1939, at the suggestion of C. E. Boord, Ohio State University. The goal was the preparation of 2,3,5-trimethylhexane and 2,3,3,4-tetramethylpentane. The reaction yielded about 18 parts of the former to 1 part of the latter. These two hydrocarbons prob-

ably resulted from the action of the Grignard reagent on two isomers of 2,3-dimethylchlorobutenes. These two isomers, probably were 1-chloro-2,3-dimethyl-2-butene, formed by 1,4 addition of hydrogen chloride to the diolefin, and 3-chloro-2,3,-dimethyl-1-butene, formed by 1,2 addition. The former chloride would be expected to react with isopropylmagnesium chloride to give 2,3,5-trimethyl-2-hexene, and the latter chloride to give 2,3,3,4-tetramethyl-1-pentene.

E. T. Cline [10] has made a study of this reaction, in which hydrogen bromide, rather than hydrogen chloride, was used. He obtained a ratio of alkenes of 1.6 parts of 2,3,5-trimethyl-2-hexene to 1 part of 2,3,3,4-tetramethyl-1-pentene.

15. 2,2,4-Trimethylhexane

In 1937 Brooks, Cleaton, and Carter [4] isolated an unknown nonane from the residue obtained in the distillation of isooctane (2,2,4-trimethylpentane), which was tentatively identified as 2,2,4-trimethylhexane. In order to establish the identity of this hydrocarbon, a sample of 2,2,4-trimethylhexane has been prepared, and a comparison of physical properties has been made.

Diisobutylene was oxidized by sodium dichromate as described by Whitmore, Homeyer, and Trent [37] to give trimethylacetic acid and 4,4-dimethyl-2-pentanone (methylneopentyl ketone). (The oxidation of diisobutylene isomers is discussed more fully in sections IV–22 and 23.)

To 7.0 moles of ethylmagnesium chloride in 1,400 ml of ether solution was added 742 g (6.5 moles) of 4,4-dimethyl-2-pentanone (bp 124° C at 760 mm Hg, $n_D^{20}=1.4038$) in 800 ml of dry ether. The reaction mixture was allowed to stand at room temperature for 35 hr, refluxed for 6 hr, and then worked up in the standard manner. The organic material was washed, dried, and distilled in column 4. In addition to ether and recovered ketone, 409 g (2.9 moles) of 3,5,5-trimethyl-3-hexanol, and 84 g (0.6 mole) of nonenes resulting from premature dehydration of the carbinol were obtained. The purified carbinol was dehydrated by heating with β-naphthalene sulfonic acid (1 g) to give a mixture of alkenes that boiled 127° to 132° C. The yield was 335 g (91%). This alkene mixture has been analyzed by Whitmore and Cook [35], who found by ozonolysis that it contained approximately 3 parts of 3,5,5-trimethyl-2-hexene, 1 part of 2-ethyl-4,4-dimethyl-1-pentene, and a trace of 3,5,5-trimethyl-3-hexene. All these compounds give the same alkane when hydrogenated, so no attempt was made to separate them.

The alkenes were hydrogenated, and the product filtered through silica gel and distilled in column 5. The middle 70 percent of the distillate, which distilled at a constant temperature, was redistilled in the same column; the middle 25 percent of the distillate from the latter distillation was used in the measurement of physical properties. The properties of the synthetic material are given in table 6 and are compared with those of the compound isolated by Brooks, et al. in table 4. The identity of the two is proved by data on the freezing point of the 50:50 mixture.

TABLE 4.—*Properties of 2,2,4-trimethylhexane*

Property	Synthetic material 2,2,4-trimethylhexane	Fraction from isooctane residue [4]
Boiling point at 760 mm Hg, °C	126.54	126.51
Change in boiling point with pressure, °C/mm Hg	0.0503	
Freezing point, °C	−123.4 (mp)	−129.53
Freezing point of mixture, °C	−124.19	
Refractive index n_D^{20}	1.4033	1.40312
Refractive index n_D^{25}	1.4010	
Density, g/ml D^{20}	0.7156	0.7153[a]
Density, g/ml D^{25}	.7118	

[a] The published density (0.7048) [4] of the material isolated from "isooctane residue" is in error. A recalculation of the original data gave 0.7153; redetermination gave 0.7154.

16. 2,2-Dimethyl-3-ethylpentane

The synthesis of 2,2-dimethyl-3-ethylpentane was carried out in the following steps: (a) Reaction of *t*-butylmagnesium chloride with carbon dioxide to give the "Grignard complex" of trimethylacetic acid, (b) reaction o this complex with ethylmagnesium chloride to produce 2,2-dimethyl-3-ethyl-3-pentanol, (c) dehydration of the carbinol to 4,4-dimethyl-3-ethyl-2-pentene, and (d) hydrogenation of the olefin to 2,2-dimethyl-3-ethylpentane.

To 50.2 moles of *t*-butylmagnesium chloride in 18 liters of ether, cooled to 5° C, was added 3 kg of solid carbon dioxide in small pieces while the reaction mixture was being stirred. Stirring was continued while the mixture came to room temperature and while it was heated to reflux for 2 hr. It was then cooled, and 104 moles of ethylmagnesium chloride in 20 liters of ether was added

slowly. After addition was complete, the mixture was stirred for 6 hr and allowed to stand at room temperature for 2 days. The product was distilled in column 6. From this distillation was obtained 3,485 g (48.2% yield) of carbinol (bp 90° to 95° C at 50 mm Hg, 171° to 176° C at 756 mm Hg, $n_D^{20}=1.4417, d^{20}=0.851$). The carbinol was dehydrated by heating with β-naphthalene sulfonic acid to give 3,600 ml of alkene. Fractionation of the crude alkene in column 5 gave 2,680 ml of purified 4,4-dimethyl-3-ethyl-2-pentene. The alkene was hydrogenated and the product filtered through silica gel and distilled in column 1. From this distillation 1,650 ml of constant-boiling 2,2-dimethyl-3-ethylpentane ($n_D^{20}=1.41225$ to 1.41230) was obtained.

17. 2,4-Dimethyl-3-ethylpentane

Preparation of 2,4-dimethyl-3-ethylpentane was accomplished by hydrogenation of the alkenes that resulted from the dehydration of 2,4-dimethyl-3-ethyl-3-pentanol. The carbinol resulted from the action of ethylmagnesium chloride on 2,4-dimethyl-3-pentanone (diisopropyl ketone).

To 76.2 moles of ethylmagnesium chloride was added 75 moles of 2,4-dimethyl-3-pentanone during 2 days. The product was recovered by addition of ice and ammonium chloride to the reaction mixture, and by subsequent distillation gave 5,650g (52.3%) of 2,4-dimethyl-3-ethyl-3-pentanol. A pure sample was obtained by redistillation of the best portion of the crude.

The carbinol was dehydrated with β-naphthalene sulfonic acid to give 6,110 ml of crude alkene mixture. A charge of 2 liters of the dehydration product was fractionated in column 5 for analysis. The individual olefins were recovered in the ratio of 77 percent of the lower-boiling 2, 4-dimethyl-3-ethyl-2-pentene to 23 percent of the higher-boiling 4-methyl-3-isopropyl-2-pentene. A sample of each of these isomers was redistilled for determination of physical constants. The values obtained were:

	2, 4-Dimethyl-3-ethyl-2-pentene	4-Methyl-3-isopropyl-2-pentene
Boiling point at 760 mm Hg (°C)	130.5	138.7
Refractive index n_D^{20}	1.4227	1.4349
Refractive index n_D^{30}	1.4204	1.4326
Density d^{20}	0.7433	0.7584
Density d^{30}	.7385	.7500

Hydrogenation of samples of both alkenes yielded the same alkane. The alkene mixture (bp 128° to 140° C) was hydrogenated and the resulting product distilled in column 4. The portion boiling 136° to 139° C was filtered through silica gel and refractionated in column 1.

In 1945 the preparation was repeated on a somewhat larger scale. For this preparation, 2,4-dimethyl-3-pentanone was fractionated in still 11. Only the purest fractions obtained (bp 124.6° to 124.7° C, $n_D^{20}=1.4015$ to 1.4017) were used in the subsequent synthesis. The carbinol was the product of reaction of the Grignard reagent prepared from 260 moles of ethyl chloride with 223 moles of redistilled ketone. The reaction product was distilled in column 21 until the head temperature was 130° C. A sample (1,600 g) of the residue was distilled in column 4. From this distillation there was obtained 1,130 g of pure carbinol (2,4-dimethyl-3-ethyl-3-pentanol) (bp 94.5° to 95.0° C at 47 mm Hg) and about 200 g of less pure material. A sample from the heart of this distillation was reserved for physical-constant measurements.

The rest of the undistilled residue was dehydrated with β-naphthalene sulfonic acid, and the dehydration products were washed, dried, and distilled in column 11. Analysis of the distillation curve showed the presence of 77 volume percent (13.4 liters) of lower-boiling olefin, and 23 volume percent (4.0 liters) of the higher-boiling isomer. In this distillation a best sample from each of the plateaus was reserved and redistilled in column 17 for physical-constant measurements.

Hydrogenation of the olefins was carried out as previously described. The paraffin was fractionated in columns 17, 18, 19, and 20. There was obtained 11,800 ml of pure hydrocarbon for engine tests.

Physical constants of materials synthesized in this later preparation are given in table 6.

18. 2,2,3,3-Tetramethylpentane (Tetrane)

The synthesis of 2,2,3,3-tetramethylpentane (a new compound, named tetrane) involved (a) preparation of 2,3,3-trimethyl-2-butanol (triptanol) from 3,3-dimethyl-2-butanone (pinacolone) and methylmagnesium bromide, (b) reaction of this carbinol with hydrochloric acid to give 2-chlor-2,3,3-trimethylbutane (triptyl chloride), and (c) reaction of the chloride with ethylmagnesium chloride to

give the nonane and 2,3,3-trimethyl-1-butene (triptene).

From 82 moles of pinacolone and 84 moles of methylmagnesium bromide, 56.5 moles of 2,3,3-trimethyl-2-butanol was prepared. This carbinol was dissolved in ether, and the solution was shaken with several portions of concentrated hydrochloric acid. Samples of the ether solution were removed periodically. The sublimation point of the crude chloride from these samples rose to 131° to 133° C. Recystallized chloride was found to sublime at 133° C. The chloride solution was washed, dried, and added to 115 moles of ethylmagnesium chloride. The mixture was stirred for 3 hr and then allowed to stand for 4 weeks at room temperature.

After the reaction mixture was worked up, the organic material was distilled in column 6, and yielded 2,100 ml of recovered triptene (trimethylbutene) and 1,900 ml of crude 2,2,3,3-tetramethylpentane, which was contaminated by a considerable amount of triptanol. The carbinol was filtered off as the hydrate, and the filtrate was dried and filtered through silica gel. The volume of nonane recovered was 1,250 ml, which represents a yield of 9 percent, based on the original pinacolone. Distillation of this material in column 4 gave 1,087 ml of hydrocarbon, which was collected at 88.6° to 88.7° C at 159 mm Hg. A portion of this material was recrystallized repeatedly, until the refractive index and freezing point were unchanged by further crystallization. Physical constants were determined on this sample.

A second run of this preparation was made later, in which recrystallized triptyl chloride was reacted with an equimolar quantity of the Grignard reagent. In this case the yield was increased to 22 percent, based on the chloride.

On authority of the National Advisory Committee for Aeronautics, procurement of 10 gallons of this hydrocarbon was undertaken in 1941. Part of this (2.9 gallons) was prepared at Ohio State University under NACA contract. The rest was prepared at the Bureau. This large-scale preparation was carried out by a modification of the technic developed at Ohio State University (C. E. Boord and K. W. Greenlee) as a part of the NACA contract. The chloride was added to the Grignard reagent in eight equal portions, in 8 successive days, while the reaction mixture was kept at 35° C. No coupling catalyst was used. (Iodine was used at O. S. U.)

An improved method was devised for the preparation of the large quantities of triptyl chloride necessary for this synthesis. The equipment consisted of three reactors, made from 30-in. lengths of 12-in. pipe, closed at both ends with companion and blind flanges. One end of each reactor was fitted with a small steel valve (¼ in.). These reactors were refrigerated (−30° C) and were connected to a manifold through which hydrogen chloride could be admitted to each. The reactors were charged with triptene in wide-mouthed bottles and mason jars. The flanges of the reactors were secured by bolts, and the reactors were allowed to stand until cold. Hydrogen chloride was then admitted until the pressure was 100 to 120 lb/in². The pressure gradually fell as the gas reacted until the pressure was about 50 to 60 lb/in². Then the process was repeated until there was no appreciable change in pressure during 1 hr. The excess gas was released, the system purged with dry air, and the product removed. The yield was practically quantitative. The product was uncolored and contained a small amount of excess hydrogen chloride. This excess was converted to alkyl chloride by adding a small amount of olefin to each jar and allowing to stand until reacted. By means of this technic, 20 to 35 liters of triptene was converted to the chloride in 1 working day. The triptene for this work was kindly supplied by the General Motors Research Laboratories, through the courtesy of T. A. Boyd and W. G. Lovell.

To 300 moles of ethylmagnesium chloride there was added 300 moles of triptyl chloride in eight equal portions during 8 days. During this time, the reaction mixture was heated to reflux temperature and stirred. At the end of 2 to 4 additional days, when all of the Grignard reagent had reacted, the mixture was worked up with ice and hydrochloric acid and washed four times with water. Distillation of the ether, and of most of the triptene, was carried out from the reaction kettle. The distillate was dried and redistilled in column 12 or 13 for recovery of triptene.

The residue in the reaction kettle was boiled with sodium propylate in propyl alcohol until the product was substantially free of chloride. After the product was washed, it was steam distilled, and the distillate dried and boiled with alcoholic silver nitrate to remove the last traces of chloride.

Then the product was filtered, washed several times, dried, and distilled in columns 11, 18, 19, and 20.

From two runs as described above, which were worked up together, there was obtained 14.92 kg (116.6 moles) of tetrane, which was 99.6 mole percent pure. This represents a yield of 19.4 percent. A total of 21.7 kg was prepared by this method.

19. 2,2,3,4-Tetramethylpentane and 2,3,3,4-Tetramethylpentane

Thd first preparation of these two nonanes was accomplished by hydrogenation of the alkenes [38] formed by the dehydration of 2,2,3,4-tetramethyl-3-pentanol. The carbinol was prepared by the reaction between methylmagnesium bromide and 2,2,4-trimethyl-3-pentanone. This ketone was the result of oxidation of 2,2,4-trimethyl-3-pentanol, one of the products resulting from the action of *t*-butylmagnesium chloride on isobutyraldehyde.

2,2,4-Trimethyl-3-pentanol was prepared by the method of Whitmore and Laughlin [38]. To 55 moles of *t*-butylmagnesium chloride was added 3,960 g (55 moles) of isobutyraldehyde. Distillation of the organic reaction products gave 4,290 g (33 moles, 60% yield) of 2,2,4-trimethyl-3-pentanol. The carbinol was oxidized to pentamethylacetone (2,2,4-trimethyl-3-pentanone) with potassium dichromate and sulfuric acid, by the method of Faworsky [15]. From 32 moles of carbinol there was obtained 3,150 g (24.6 moles, 77% yield) of ketone, which was distilled in column 5.

The 2,2,4-trimethyl-3-pentanone (24.6 moles) in 6 liters of ether was reacted with 26 moles of methylmagnesium bromide, and the product was distilled in column 5 until the temperature reached 143° C. At this point dehydration of the carbinol was beginning to take place, so the distillation was interrupted, and the clear, slightly yellow residue (2,950 ml) was dehydrated with β-naphthalene sulfonic acid.

From the dehydration there resulted 2,410 ml of alkene mixture, which was dried and distilled in column 3. The following fractions were obtained:

Fraction	Boiling range	Volume	
	°C	ml	
1	91 to 119	23	forerun.
2	119 to 124	1,550	3,3-dimethyl-2-isopropyl-1-butene.
3	124 to 129	200	intermediate.
4	130 to 135	600	2,3,3,4-tetramethyl-1-pentene.
5	>135	120	residue.

Fractions 2, 3, and 4 represents a combined yield of alkenes of 15.9 moles (65%, based on 2,2,4-trimethyl-3-pentanone). Samples from the middle of the plateaus represented by fractions 2 and 4 were reserved for physical-constant measurements. No attempt was made to isolate 2,3,4,4-tetramethyl-2-pentene, a very small quantity of which was found by Whitmore and Laughlin [38].

The alkene fraction, which distilled at 119° to 124° C, was hydrogenated, and the product was filtered through silica gel and distilled in column 3. There was obtained 1,070 ml of hydrocarbon, which boiled 133.7° to 134.1° C, n_D^{20} (uncorrected) = 1.4147 to 1.4150. Redistillation of this material gave 930 ml collected at 133.8° C. Physical constants were determined on a sample from the center of this fraction.

Alkene fraction 4 was treated in like manner, and yielded 347 ml of material collected at 142° C (uncorrected), fractions of which showed a refractive index range, n_D^{20} (uncorrected) of 1.4219 to 1.4220 A sample from this distillation was reserved for determination of physical constants.

All intermediate fractions, foreruns, residues, and material eluted from silica gel were hydrogenated and distilled in column 8. In this way there was obtained an additional 200 ml of 2,2,3,4-tetramethylpentane and 145 ml of 2,3,3,4-tetramethylpentane.

Tests on these two hydrocarbons demonstrated the advisability of preparing larger quantities. Consequently, 10 gallons of each was synthesized at Pennsylvania State College, under the direction of Frank C. Whitmore, by contract with the NACA.

These hydrocarbons were purified in these laboratories for engine tests by distillation in column 1. New pure samples for measurement of physical constants were obtained concurrently.

20. Dimethyl Zinc Synthesis of Three Tetramethylpentanes

The syntheses of three tetramethylpentanes are described in the preceding sections. In the spring of 1942 considerable interest was developed in dimethyl zinc syntheses. It was demonstrated that the engine characteristics of a fuel derived from butene co-dimer could be considerably improved by the introduction of tetramethylpentanes. This was first accomplished by synthesis of these nonanes *in situ*. An olefin co-polymer fraction containing 3,4,4-trimethyl-2-pentene and 2,3,4-trimethyl-2-pentene was reacted with dry hydrogen chloride until about 60 percent of the olefin was converted to chloride. This chloride-olefin mixture was treated with dimethyl zinc in a solvent of hydrogenated co-dimer, which contained 2,2,3- and 2,3,4-trimethylpentanes. The resultant product was hydrogenated to a mixture of hydrocarbons, all known to have superior characteristics.

This study led to the syntheses of these compounds in a pure state by this method.

Secondary and tertiary butyl alcohols were co-polymerized in the presence of sulfuric acid in the manner described by Whitmore, Laughlin, Matuszeski, and Surmatis [39]. A portion of the product was analyzed by distillation in column 1 and was found to contain the "diisobutylenes", (2,4,4-trimethyl-1-and 2-pentenes) (25%), 3,4,4-trimethyl-2-pentene (23%), 2,3,4-trimethyl-2-pentene (37%), and higher-boiling material (15%). The rest of the olefin mixture was roughly separated by distillation in column 5. The fractions which boiled 107° to 120° C amounted to 9,740 g, and consisted of 2,3,4-trimethyl-2-pentene and 3,4-4-trimethyl-2-pentene as major components. Part of this fraction (6,300 g) was fractionated in column 2. By this distillation there was obtained 1,150 g of 3,4,4-trimethyl-2-pentene (n_D^{21}=1.4230, n_D^{25}=1,4205, D^{20}=0.7392, D^{25}=0.7350, bp 112.1° to 112.8° C) and 1,865 g of 2,3,4-trimethyl-2-pentene (n_D^{25}=1,4275, n_D^{25}=1,4250, D^{20}=0.7434, D^{25}=0.7391, bp 116.3° to 116.5° C).

These two alkenes were reacted separately with hydrogen chloride at −60° C in an apparatus previously described [19] (also section IV–3) until approximately 60 percent of the alkene had been converted to alkyl chloride. The products were washed, dried, and fractionated in column 3. In this way, 716 g of constant-boiling 3-chloro-2,2,3-trimethylpentane was obtained from the 3,4,4-trimethyl-2-pentene. The chloride from 2,3,4-trimethyl-2-pentene (1,410 g) was probably a mixture of 2-chloro-2,3,4-trimethylpentane and 3-chloro-2,3,4-trimethylpentane. As these two chlorides were expected to yield two different nonanes (by reaction with dimethyl zinc) which have boiling points differing by about 8° C, no attempt was made to separate the chloride mixture. Physical constants measured on the chlorides are included in table 6.

(a) 2,2,3,3-Tetramethylpentane

In the apparatus, and by the technic described in section IV–3, 4.15 moles (614 g) of 3–chloro-2,2,3-trimethylpentane in 700 ml of isooctane (2,2,4-trimethylpentane, S–4 reference fuel) were allowed to react with the dimethyl zinc from 7.75 moles of methyl iodide. The dimethyl zinc was in a solution with 500 ml of "isooctane". The bath temperature for the reaction was 7° C. The product was boiled for 2 hr with 5 percent potassium hydroxide in alcohol, washed, and fractionated in column 4. This distillation gave:

Fraction No.	Boiling range	Volume	Refractive index (n_D^{20})
	°C	ml	
1	96 to 100	1130	1.3918
2	100 to 110	65	1.4059
3 and 4	110 to 116	231	1.4195 to 1.4225
5	116 to 138.6	27	1.4226
6	138.6 to 140.3	39	1.4226
7	140.3	150	1.4233
8*	140.3	77	1.4232
9 (residue)*	>140.3	10	1.4379

* Distillation of the residue from fraction 7 was continued in still 8 and gave the values shown.

Fraction 1 was recovered solvent. Alkene byproducts of the reaction, formed by dehydrochlorination of the alkyl chloride, were contained in fractions 2 to 5. By the low refractive indices of these fractions, it is indicated that this material consisted mostly of 3,4,4-trimethyl-2-pentene. The yield of 2,2,3,3-tetramethylpentane (fractions 6, 7, and 8) amounted to 37.7 percent based on alkyl chloride. Fraction 7, after filtration through silica gel, had the following properties: Freezing point, −11.85° C; boiling point, 140.20° to 140.23° C

at 760 mm Hg; refractive index, $n_D^{20}=1.4233$, $n_D^{25}=1.4211$; density, $d^{20}=0.7565$, $d^{25}=0.7527$. It may be seen that the product was of high purity, when these properties are compared with those of the pure sample, as listed in table 6. The freezing point indicates a purity of about 99.5 mole percent.

(b) 2,2,3,4- and 2,3,3,4-Tetramethylpentanes

By using the same procedure described above, two runs were made in which a total of 8.35 moles of the mixture of 2-, and 3-chloro-2,3,4-trimethylpentanes was reacted, at 10° C, with the dimethyl zinc from 15.5 moles of methyl iodide. The combined products were refluxed with alcoholic potassium hydroxide, washed, dried, and distilled in column 4. This operation gave:

Fraction No.	Boiling range	Volume	Refractive index (n_D^{20})
	°C	ml	
1	95 to 100	2,051	1.3917
2	100 to 115	116	1.4080
3 and 4	115 to 119	440	1.4269 to 1.4267
5	119 to 130	31	1.4219
6 to 8	130.0 to 133.5	139	1.4158 to 1.4150
9	133.5 to 134.0	138	1.4152
10	134 to 140	64	1.4183
11*	140.0 to 141.5	10	1.4212
12*	141.5 to 142.0	60	1.4218
13*	142.0 to 143.0	20	1.4221
14*	143 to 165	10	1.4271
15 (residue)*		83	1.4570

* The residue was distilled in still 8, and gave the values shown.

Fraction 1 was recovered "isooctane," fractions 3 and 4 were alkene byproducts, indicated to be mostly 2,3,4-trimethyl-2-pentene by the refractive indices. The total yield of tetramethylpentanes (fractions 6 to 14) amounted to 30 percent, based on alkyl chloride. These tetramethylpentanes consisted of about 71 percent of 2,2,3,4-tetramethylpentane and about 29 percent of 2,3,3,4-tetramethylpentane.

Fraction 9, after filtration through silica gel, had the following properties: Freezing point, −122.54° C; boiling point 133.3° to 133.4° C at 760 mm Hg; refractive index, $n_D^{20}=1.4148$, $n_D^{25}=1.4127$; density, $d^{20}=0.7397$, $d^{25}=0.7358$. These values are in agreement with those reported for the pure 2,2,3,4-tetramethylpentane (table 6).

Fraction 12 was filtered through silica gel, and the eluent was used for the measurement of physical properties. The following properties were found: Boiling point, 141.3° to 141.4° C at 760 mm Hg; refractive index, $n_D^{20}=1.4217$, $n_D^{25}=1.4196$; density, $d^{20}=0.7545$, $d^{25}=0.7512$. These data agree with those reported for purer 2,3,3,4-tetramethylpentane in table 6.

A tetramethylpentane, assumed to be 2,3,3,4-tetramethylpentane, was prepared by Dinerstein [11] in 1940, by action of dimethyl zinc on "3-chloro-2,3,4-trimethylpentane." Later work [14, 31] shows that the hydrocarbon prepared by Dinerstein was 2,2,3,4-tetramethylpentane.

21. 2,4-Dimethyl-3-isopropylpentane (Triisopropylmethane)

The recent preparations of triisopropylcarbinol by the action of isopropyl lithium on 2,4-dimethyl-3-pentanone (diisopropyl ketone) [42], and by the action of isopropyl chloride on diisopropyl ketone in the presence of sodium [3], have made available a method for synthesizing triisopropylmethane (2,4-dimethyl-3-isopropylpentane). A quantity of this compound has been prepared by the use of isopropyl lithium.

Preliminary work on this reaction was performed in several small-scale experiments, in each of which 10 gram atoms of lithium, 6.5 moles of isopropyl chloride, 5.4 moles of diisopropyl ketone, and 2,000 ml of solvent were used. During this study, it was found that technical 2,2,4-trimethylpentane (isooctane) served admirably as a solvent when its use was augmented by efficient stirring and external cooling of the reaction mixture. No preliminary purification of the solvent was necessary, and the hazards accompanying its use are much less than those of the petroleum ether used by the original investigators [42].

The preparation of the considerable quantities of finely divided lithium required was expedited by the use of a small laboratory rolling mill. While the lithium was being worked in the mill it was lubricated and coated with a mixture of 80 percent isooctane and 20 percent light mineral oil applied by means of an oil can. This technic tended to prevent the lithium from sticking to the rolls and also prevented excessive oxide formation. The rolled pieces, about 0.003 in. thick, were cut into ribbons and then into squares in a large shallow pan under isooctane.

The yields in all the preliminary runs amounted to 18 to 22 percent of carbinol. No appreciable change in yield was experienced when the reaction

between isopropyl lithium and diisopropyl ketone was carried out at 99°C, the temperature of boiling isooctane, rather than at 35° C, the temperature used by the original investigators.

After the technic of handling the reaction had been sufficiently developed, a large run was carried out in the 50-gallon stainless-steel kettle. The total quantity of reactants used were: 159 g atoms (1.10 kg) of lithium, 115 moles (9.03 kg) of isopropyl chloride, 80 moles (9.13 kg) of diisopropyl ketone, and 55 liters of isooctane. The quantity of isopropyl chloride was relatively larger than that used by the original investigators in order that a minimum amount of lithium be left unreacted, and to compensate for possible loss through the reflux condenser. The diisopropyl ketone was constant-boiling material obtained by redistillation of the commercial product in still 11.

The kettle was flushed with nitrogen and charged with 31 liters of isooctane. About half the lithium was added and the reaction started by the addition of 1 liter of isopropyl chloride in 1 liter of isooctane and by warming the jacket to 35° C. The remainder of the lithium was added in three additional charges during the next 2½ days. During the first 3 days, a mixture of the remainder of the isopropyl chloride in an equal volume of isooctane was added in four charges.

A solution of diisopropyl ketone in 11.4 liters of isooctane was added during 8 hr, while the reaction temperature was held at 45° to 60° C. After addition was complete, the mixture was warmed and stirred for 5 hr, after which it was cooled. Decomposition of the reaction mixture was effected by the addition of 25 pounds of cracked ice, followed by a solution of 11 pounds of ammonium chloride in 5 gallons of water. The aqueous layer was removed, and the organic layer washed five times, each time with 3 to 5 gallons of water, after which it was withdrawn and dried overnight with potassium carbonate.

Fractionation of the product in column 6 gave: recovered isooctane; diisopropyl ketone, bp 121° to 126° C, 2,355 g; intermediate fractions, 240 g; and triisopropylcarbinol, bp 104° to 110° C at 50 to 55 mm Hg, 2,576 g. This represents a yield of 20.4 percent, based on the diisopropyl ketone added. A part of the triisopropylcarbinol was redistilled and a pure sample collected from the middle of this distillation for the measurement of physical constants.

The carbinol was dehydrated by distillation from anhydrous copper sulfate. From 16 moles of triisopropylcarbinol, 14.4 moles (90%) of crude 2,4-dimethyl-3-isopropyl-2-pentene was obtained. Water recovery amounted to 80 percent. The crude olefin was dried over calcium chloride and distilled in column 6, from which 1,372 g of material that boiled 153.2° to 153.6° C at 756 to 759 mm Hg, n_D^{20}=1.4368 to 1.4371 (all values uncorrected) was collected. A sample was removed from the middle of the distillation for the measurement of physical constants.

The olefin was hydrogenated, and distilled in column 6, and gave 1,100 g (80%) of "constant-boiling material;" bp 156.5° C at 749 mm Hg; n_D^{20}=1.4234−1.4236 (all values uncorrected). This material contained a trace of olefin, which was removed by repeated filtration through silica gel. Refractionation under reduced pressure afforded the means of obtaining a pure sample for physical-constants measurements.

22. Pentamethylpentanes

(a) 2,2,3,3,4-Pentamethylpentane

The first preparation of 2,2,3,3,4-pentamethylpentane was carried out by the reaction between 2-chloro-2,3,3-trimethylbutane and isopropylmagnesium chloride.

To 30.5 moles of isopropylmagnesium chloride in 10.53 liters of ether solution there was added, at room temperature, 26.4 moles of 2-chloro-2,3,3-trimethylbutane (sublimation point 132.7° to 134° C) in 3.5 liters of ether. After standing for 3 weeks at 15° to 20° C, the reaction mixture was worked up in the usual manner. The product, distilled in column 6, gave 14.8 moles of 2,3,3-trimethyl-1-butene, formed by dehydrochlorination of 2-chloro-2,3,3-trimethylbutane; 0.1 mole of 2-propanol, formed by oxidation of the Grignard reagent found in an azeotrope with 2,3,3-trimethyl-1-butene; 2.2 moles of recovered 2-chloro-2,3,3-trimethylbutane; 3.1 moles of 2,3,3-trimethyl-2-butanol, presumably by hydrolysis of the chloride; and 1.05 moles of crude 2,2,3,3,4-pentamethylpentane. This represents a yield of 4.0 percent. Another run, in which 19.3 moles of the chloride was used, and which was kept at 5° C for 3 weeks, then at room temperature for 2 weeks, yielded 0.6 mole of additional crude (3.1 percent yield).

The combined yield of crude material (300 ml) was fractionated in column 8. From this distilla-

tion there was obtained 226 ml of material that boiled at 163.7° to 164° C (uncorrected). This product was redistilled in the same column, and there was collected 186 ml of constant-boiling, constant-refractive index material. The physical constants of this product, after filtration through silica gel were as follows: fp −37.5° C, n_D^{20}=1.4361, d^{20}=0.7803, bp 165.54° to 165.56° C at 750.5 mm Hg.

Later, two other methods for the preparation of this decane were investigated. Both of these methods involved the methylation of 3-chloro-2,2,3,4-tetramethylpentane. This chloride was prepared in good yield from the corresponding alcohol by reaction with concentrated hydrochloric acid. The chloride decomposed easily when a boiling-point determination was attempted at atmospheric pressure. It would not crystallize at dry-ice temperature and had an index of refraction (n_D^{20}) of 1.4389. The carbinol was prepared by the reaction between methylmagnesium bromide and 2,2,4-trimethyl-3-pentanone (see section IV–19).

In one experiment on the methylation of this chloride, 1.7 moles of the chloride in 320 ml of benzene was added to 2.5 moles of dimethyl zinc, using the previously described technic. Distillation analysis of the product of reaction showed the presence of 0.4 mole (23.5%) of 2-isopropyl-3,3-dimethyl-1-butene, and 0.81 mole (47.5%) of 2,3,3,4-tetramethyl-1-pentene, both formed by dehydrochlorination of the alkyl chloride. In addition, there was found 0.38 mole (assuming $C_{10}H_{22}$) of material that boiled 150° to 160° C, and from which no pure material could be isolated.

In another experiment 10.7 moles of 3-chloro-2,2,3,4-tetramethylpentane was treated with 11.0 moles of methylmagnesium bromide in ether solution. The reaction was allowed to take place over a period of 3 weeks at 15° to 22° C. The products of the reaction, was determined by distillation analysis, consisted of 3.0 moles (28%) of 2-isopropyl-3,3-dimethyl-1-butene, and 5.7 moles (53%) of 2,3,3,4-tetramethyl-1-pentene, formed by dehydrochlorination of the alkyl chloride. In addition, there was found 0.5 mole (4.7%) of crude 2,2,3,3,4-pentamethylpentane. (Boiling range=158° to 167° C, n_D^{20}=1.4354 to 1.4369.)

It is interesting to note that in both of these trials, the dehydrochlorination of the alkyl chloride led to approximately the same relative proportions of the two nonenes, namely, 1 part of 2-isopropyl-3,3-dimethyl-1-butene and 2 parts of 2,3,3,4-tetramethyl-1-pentene. This proportion is not the same as occurs when the carbinol itself is dehydrated. In that case the proportions are 1 parts of 2-isopropyl-3,3-dimethyl-1-butene and 1 part of 2,3,3,4-tetramethyl-1-pentene [31, 38].

(b) Pentamethylpentanes from 2,2,3,4,4-Pentamethyl-3-pentanol (trial 1)

In an attempt to prepare 2,2,3,4,4-pentamethylpentane, it has been found that 2,2,3,4,4-pentamethyl-3-pentanol will dehydrate under the influence of iodine to a mixture of two decenes which, on hydrogenation, yields both of the pentamethylpentanes.

In 1933 Whitmore and Laughlin [38] reported the dehydration of 2,2,3,4,4-pentamethyl-3-pentanol by means of β-naphthalene sulfonic acid to give 2-*t*-butyl-3,3-dimethyl-1-butene without appreciable rearrangement. They also reported a small amount of low-boiling, unidentified material.

As this reaction offered a means of preparing 2,2,3,4,4-pentamethylpentane, a trial run was made. When the carbinol was dehydrated with β-naphthalene sulfonic acid at atmospheric pressure, the products of the reaction consisted of isobutylene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, and only a small amount of higher boiling material. No 3,3-dimethyl-1-butene was found in the reaction products.

Dehydration of the carbinol with iodine was found to yield a mixture of decenes, comprising of 2-*t*-butyl-3,3-dimethyl-1-butene and 2,3,3,4-pentamethyl-1-pentene.

(1) *Preparation of 2,2,4-trimethyl-3-pentanone and 2,2,4,4-tetramethyl-3-pentanone.*—2,2,4-Trimethyl-3-pentanone was prepared by the Hall-Bauer synthesis [17], in toluene solvent by the action of sodium amide and then methyl sulfate on 2,4-dimethyl-3-pentanone. Sodium amide was made in 90- to 94-percent yield by the method described in Organic Syntheses [29]. The crude 2,2,4-trimethyl-3-pentanone was methylated a second time by the same method to give 2,2,4,4-tetramethyl-3-pentanone. The manipulative details of these reactions are described by Whitmore and Laughlin [38]. The over-all yield was 45 percent of that theoretically possible, calculated without including recovered 2,4-dimethyl-3-pen

ne and 2,2,4-trimethyl-3-pentanone, which were ecycled in the synthesis.

Part of the 2,2,4 trimethyl-3-pentanone used in is synthesis was prepared at Pennsylvania State ollege (F. C. Whitmore), the rest was synthesized the Bureau as described. A charge of this tone was fractionated in column 1 for the isola- on of a pure sample for physical-constant meas- rements. In the same column, a sample of the 2,4,4-tetramethyl-3-pentanone was also distilled r the same purpose.

(2) *Preparation of 2,2,3,4,4-pentamethyl-3-pentanol.*—A solution of 10 moles of methylmagnesium omide was reacted with 8.75 moles of 2,2,4,4- tramethyl-3-pentanone and the product worked p in the usual manner. Fractionation of the oduct in column 4 at a pressure of 57 mm Hg ve a forerun of 307 ml of material that boiled low 105° C. At this point the carbinol began solidify in the condenser, and the pale-yellow aterial remaining in the pot was found to be ite pure carbinol (melting point above 37° C). portion was recrystallized from ether for use in e determination of physical properties. The ld amounted to 75 percent of the theoretical antity.

(3) *Dehydration of 2,2,3,4,4-pentamethyl-3-pentanol with β-naphthalene sulfonic acid.*—Dehydra- n of 897 g (5.7 moles) of 2,2,3,4,4-penta methyl- pentanol with 8 g of β-naphthalene sulfonic acid der a fractionating column resulted in the dis- lation of a water layer, an organic layer (855 ml), d about 50 ml of material collected in a dry-ice p. The organic layer which smelled strongly sulfur dioxide and hydrogen sulfide, was washed, ied, and distilled from sodium, and gave the llowing fractions:

Fraction No.	Head temperature	Volume	Refractive index (n_D^{20})
	°C	ml	
	<54	4	
	54 to 57	65	1.3908
	51 to 71	26	1.4033
	71 to 73	23	1.4084
	73 to 75	365	1.4100
	75 to 150	35	1.4223
	150 to 153.2	24	1.4375
	153.2 to 156.5	33	1.4400
	156.5 to 157	14	1.4411
	>157	22	

Distillation interrupted.

A considerable quantity of gas was evolved during the distillation. This gas boiled at about −4° C, was readily absorbed in sulfuric acid, and absorbed bromine. Regeneration from sulfuric acid solution by neutralization resulted in *t*-butyl alcohol. This identifies the gas as isobutylene. The other principal products of the reaction were fraction 2 (2,3-dimethyl-1-butene), fraction 5 (2,3-dimethyl-2-butene), and fractions 7 and 8, which probably contained a mixture of 2,3,3,4,4-pentamethyl-1-pentene and 2-*t*-butyl-3,3-dimethyl-1-butene. As the products of this distillation did not yield the desired compounds in any appreciable quantity, more elaborate analysis was not undertaken.

(4) *Dehydration of 2,2,3,4,4-pentamethyl-3-pentanol with iodine.*—A charge of 2,2,3,4,4-pentamethyl-3-pentanol (640g, 4.1 moles) was refluxed with 4 g of iodine, and the product was distilled through a short fractionating column, yielding 70 ml of water and 700 ml of organic material. The organic layer was washed, dried, and fractionated roughly. The distillate from three runs were combined, yielding 1,950 ml of material, which, on further fractionation, gave 1,800 ml that boiled at 140° to 155° C. The residue was semisolid and had an odor similar to that of a carbinol. The 140° to 155° C fraction was redistilled into the following fractions:

Fraction No.	Head temperature	Volume	Refractive index (n_D^{20}) (uncorr.)
	°C	ml	
1	100 to 148.2	55	1.4314
2	148.2 to 149.0	43	1.4348
3	149.0 to 149.6	283	1.4355
4	149.6 to 151.0	460	1.4355
5	151.0 to 152.0	190	1.4367
6	152.0 to 153.0	55	1.4381
7	153.0 to 155.0	50	1.4396
8	155.0 to 157.0	26	1.4410

A constant-boiling portion of fraction 3 was reserved for determination of physical constants and ozonolysis. At 157° C, solid material started to form in the condenser, so the distillation was stopped. The cooled residue in the flask was solid, melting at 34.5° to 37.5° C, but a mixture of this compound and the original carbinol was liquid at room temperature. The material was soluble in ether, insoluble in water, slightly

soluble in 85 percent phosphoric acid, and was unaffected by sodium.

Analysis showed the presence of 83.1 percent of carbon and 13.8 percent of hydrogen.[5] Because of the volatility of the compound, these results may be low. By extending the C-H content to total 100 percent, the analysis was calculated to be 85.8 percent of carbon and 14.2 percent of hydrogen, which agrees with the analysis of an alkene. The molecular weight was found cryoscopically to be 142.4 (theory for $C_{10}H_{20}$=140.2).

At this point the distillation of the solid olefin was continued after provision had been made to prevent solidification of material in the condenser. This distillation gave the following fractions:

Fraction No.	Head temperature	Weight
	(° C)	(g)
9	157.0 to 157.2	30.1
10	157.2 to 158.0	18.6
11	158.0 to 158.2	18.4
12	158.2	27.7
13	158.2 to 158.9	28.1
14	158.9 to 159.0	28.3
15	159.0 to 159.0	28.2
Residue		39.1

Ozonolysis was performed on fraction 15.

(5) *Ozonolysis of alkenes.*

(a) LOWER-BOILING ALKENE (2-*t*-BUTYL-3,3-DIMETHYL-1-BUTENE). Ozonization of 0.21 mole of alkene in 300 ml of isopentane at —5° to —10° C was accomplished in 12 hr. Oxygen containing 7.5 percent of ozone was used at the rate of 7,500 ml/hr. The solvent was not removed prior to decomposition because the ozonide proved to be a solid. Decomposition was effected by means of the technic developed by Whitmore and Church [34]. The reaction was of medium violence and gave rise to 36.5 ml of oil and 150 ml of water layer. Analysis of the water layer showed the presence of 0.18 mole of formaldehyde, and no other low molecular weight aldehyde or ketone. The oil was distilled to yield 24.3 ml of 2,2,4,4-tetramethyl-3-pentanone (boiling point 150° to 155° C), which, when treated with methylmagnesium bromide, gave 2,2,3,4,4-pentamethyl-3-pentanol, the identity of which was proved by a mixed melting point with a known sample.

(b) HIGHER-BOILING ALKENE (2,3,3,4,4-PENTAMETHYL-1-PENTENE). In the same manner as described above, 0.11 mole of the higher-boiling alkene was ozonized in 300 ml of isopentane at —10° to —20° C to yield 0.071 mole of formaldehyde and 9 g of an oil (boiling point 172° C, n_D^{24}=1.4149). This oil gave a positive iodoform test, and was oxidized by 50 percent nitric acid to 2,2,3,3-tetramethyl butanoic acid [22, 23]. After several crystallizations from alcohol, this acid melted at 196° to 197° C, the same value reported by Whitmore, Marker, and Plambeck, Jr. [41]. The neutral equivalent was found to be 147.3. The amide was prepared and found to melt at 201.5° to 202° C, which agrees with the melting point found by Whitmore, et al. [41] (201° to 202° C). The ketone gave a 2,4-dinitrophenylhydrazone, which melted at 182° to 183° C. The ketone was therefore considered to be 3,3,4,4-tetramethyl-2-pentanone.

(6) *Hydrogenation of the decenes.* The crude lower-boiling alkene from the dehydration of 2,2,3,4,4-pentamethyl-3-pentanol (fractions 2 to 8, inclusive) was hydrogenated and filtered through silica gel. Distillation in column 5 gave:

Fraction No.	Boiling range	Volume	Refractive index (n_D^{20})
	° C	ml	
1 to 2	153.4 to 158.4	100	1.4296 to 1.4304
3 to 8	158.4	300	1.4306 to 1.4307
9 to 14	158.4 to 159.8	303	1.4307 to 1.4313
15 to 16	159.2 to 161.7	97	1.4320 to 1.4341
Residue		47	1.4390

An analysis of the distillation curve showed the presence of 735 ml of 2,2,3,4,4-pentamethylpentane, and 112 ml of 2,2,3,3,4-pentamethylpentane.

Hydrogenation of the higher-boiling alkene was carried out in a solvent (2,2,4-trimethylpentane). Distillation gave, in addition to the solvent, a small forerun and 247 ml of fractions collected at 163° to 164° C (n_D^{20}=1.4358 to 1.4361). The best samples of both decanes were reserved for measurement of physical constants.

The yield of alkanes isolated in the pure state (calculated on 2,2,4,4-tetramethyl-3-pentanone) amounted to 25.8 percent of 2,2,3,4,4-pentamethylpentane, and 11.4 percent of 2,2,3,3,4-pentamethylpentane. These yields could not be used to form a definite opinion of the reaction nor can much weight be placed on the ratio of products found, since a loss experienced in the distillation

[5] Thanks are due K. C. Fleischer, of this Bureau, for this microanalysis.

and handling of the higher-boiling decene is not accounted for.

(c) Pentamethylpentanes from 2,2,3,4,4-Pentamethyl-3-pentanol (trial 2)

The second run of this series of reactions was made to increase the stock of hydrocarbons and to obtain more information on the ratio of products formed by dehydration of the carbinol.

(1) *Preparation of 2,2,4-trimethyl-3-pentanone.*—For this second synthesis, an easier method was devised for making 2,2,4-trimethyl-3-pentanone. This method was an adaptation of that described by Nef [26], who obtained this ketone by the exhaustive methylation of acetone, methylisopropyl ketone, diethyl ketone, or pinacolone with methyl iodide and potassium hydroxide in a sealed tube at 140° C. The method used in the present work substituted the less expensive methyl bromide for methyl iodide in the methylation of commercial 2,4-dimethyl-3-pentanone.

Several runs of various sizes were made and the results are summarized in table 5. These reactions were carried out in hydrogenation bombs. The bomb was chilled by solid carbon dioxide and charged with the reactants, then sealed and heated to the temperature indicated. As the reaction is exothermic, it was found difficult to hold a predetermined narrow temperature range. (The operation could probably be made more efficient by pumping the methyl bromide into the reaction vessel as it is consumed by the reaction in order to obtain more stable reaction conditions.) When the reaction was complete the bomb was cooled and the contents washed well with water, dried, and fractionated. In one experiment (5–1) an attempt was made to distill the residue (247 g). It was found to contain lachrymatory materials, but little if any 2,2,4,4-tetramethyl-3-pentanone. (None of this compound was found by Nef in any of his methylation products.)

TABLE 5.—*Methylation of 2,4-Dimethyl-3-pentanone*

Run No.	Date	Methylating agent	2,4-Dimethyl-3-pentanone	Potassium hydroxide	Temperature	Duration	Yield of 2,2,4-trimethyl-3-pentanone *
		Moles	*Moles*	*Moles*	*° C*	*hr*	*Percent*
163	11- 9-44	CH_3I (1.5)	1.2	3.5	140 to 160	7.0	55
164	11-14-44	$(CH_3)_2SO_4$ (1.5)	1.2	3.5	140 to 160	7.2	0
165	11-24-44	CH_3Br (4)	4	12	160 to 170	6.0	35
166	11-27-44	CH_3Br (4)	4	12	140 to 150	9.1	15
167	12- 7-44	CH_3Br (4)	4	12	190 to 200	11.7	35
168	1-11-45	CH_3Br (4)	4	6 (CaO)	190 to 200	8.0	0
5-1	12-19-44	CH_3Br (47.7)	39.6	120	200 to 215	8.0	57
5-2	12-28-44	CH_3Br (47.7)	39.6	120	190 to 200	10.0	54
5-3	1- 4-45	CH_3Br (47.7)	39.6	120	200 to 230	8.0	47

* Based on 2,4-dimethyl-3-pentanone consumed.

(2) *Preparation of 2,2,4,4-tetramethyl-3-pentanone.*—While the preparation of 2,2,4-trimethyl-3-pentanone was in progress, a new and simpler method for synthesizing 2,2,4,4-tetramethyl-3-pentanone was described by Bartlett and Schneider [3]. This new procedure eliminated entirely the necessity of using sodium amide in the synthesis. The Bartlett and Schneider reaction involved interaction between *t*-butyl chloride, methyl trimethylacetate, and sodium sand to give a mixture of 2,2,4,4-tetramethyl-3-pentanone and 2,2,4,4-tetramethyl-3-pentanol as major products.

Several small-scale runs (1.6 to 2.0 moles) of this reaction were made. There was no appreciable difference in the yields of *di*-tertiary-butyl compounds from reactions in which technical "isooctane" (2,2,4-trimethylpentane) was used as a solvent and those in which isopentane was used. As the former solvent is considered safer, it was used in the majority of the trail runs and in the large-scale run. Slightly larger (2 to 5%) yields were obtained when sodium sand was used rather than sodium wire. In none of the small-scale runs did the yield of combined *di*-tertiary-butyl compounds exceed 53 percent. (Bartlett and Schneider report yields up to 71%). After the technic for handling this reaction had been sufficiently developed, a large run was made in the stainless-steel kettle.

(a) METHYL TRIMETHYLACETATE.—To a solution of 53 kg (177 moles) of sodium dichromate dihydrate (technical) in 98 liters of water in the

glass-lined reactor was added 39.9 liters of concentrated sulfuric acid. The solution was heated to 82° C and 6.6 kg (59 moles) of 2,4,4-trimethyl-2-pentene (97% pure, see section IV–28) was added over a period of 5 hr. The rate of addition was regulated so that the temperature of the mixture did not exceed 88° C. Then about 3 liters of methyl alcohol was added to use the excess dichromate, and the mixture was subjected to steam distillation. There was obtained thereby 5.76 kg of organic layer and about 30 liters of aqueous layer. The aqueous layer yielded, on distillation, an additional 0.82 kg of organic material. The crude product was distilled in columns 4 and 5, and yielded 3.91 kg of trimethylacetic acid (bp 160° to 165° C) (65.0% yield).

The methyl ester of trimethylacetic acid was prepared in the usual manner by refluxing a solution of the acid in methyl alcohol. Sulfuric acid was used as the catalyst.

(b) 2,2,4,4-Tetramethyl-3-pentanone.—Sodium sand, from 6.8 kg (300 moles) of sodium was prepared under toluene (22 liters) in the usual manner. The mixture was cooled to 15° C and 16 liters of technical "isooctane" (2,2,4-trimethylpentane) and 16 kg (173 moles) of *t*-butyl chloride added. After the reaction was initiated by the addition of a small quantity of ester, the remainder (total 7.98 kg, 68.5 moles) was added during 4 hr, while the temperature was maintained at 35° to 40° C. Stirring was continued for 8 hr, then the mixture was allowed to stand overnight. The product was worked up in the manner described by Bartlett and Schneider. Distillation gave 2.57 kg (18.1 moles) of 2,2,4,4-tetramethyl-3-pentanone (bp 151.5° to 156.0° C), 666 g of intermediate and 2.72 kg (18.9 moles) of 2,2,4,4-tetramethyl-3-pentanol (bp 167° to 173° C). Including the intermediate, this represents a yield of approximately 61 percent, based on methyl trimethylacetate.

The carbinol fraction and the intermediate containing carbinol were combined and oxidized in two batches. In each batch 1.36 kg (9.45 moles) of carbinol and 333 g of intermediate [6] were suspended in a solution of 1,255 g of sodium dichromate dihydrate in 1,170 ml of water. While the reaction mixture was held at 45° to 60° C, a solution of 2,300 ml concentrated sulfuric acid in 2,170 ml of water was added during 2 days, after which the reaction mixture was stirred and heated to 50° C for 1 day. The organic material was then steam distilled, dried, and fractionated. There was thereby obtained 1.35 kg (9.52 moles) of ketone (bp 151° to 154° C) (78% yield).

In the same manner, all the 2,2,4,4-tetramethyl-3-pentanol obtained in the several preliminary runs was oxidized to ketone, and all the ketone from the several sources, was combined. This included a small amount prepared by the Haller-Bauer reaction [17].

(c) Preparation and Dehydration of 2,2,3,4,4-pentamethyl-3-pentanol.—The pentamethylpentanol was prepared in the manner already described. From 6.96 kg (49.0 moles) of 2,2,4,4-tetramethyl-3-pentanone there was obtained 4.84 kg (30.6 moles) of 2,2,3,4,4-pentamethyl-3-pentanol (62.6% yield).

Dehydration of the carbinol was caused by refluxing with iodine. In a trial run, 322 g (1.98 moles) of carbinol was boiled with 3.3 g of iodine. During 2 hr, 93% of the theoretical quantity of water was eliminated and collected. The organic layer was washed with sodium thiosulfate solution and with water, dried, and distilled in column 17. The charge was 246 g. The decene fractions (bp 145° to 158.9° C) weighed 216.6 g (1.54 moles, 78%). Analysis of the distillation curve showed that these fractions consisted of equal parts of the two isomers, 3,3-dimethyl-2-*t*-butyl-1-butene and 2,3,3,4,4-pentamethyl-1-pentene.

Treatment of the main portion of the carbinol for the preparation of the pentamethylpentane followed the procedure already described.

23. 2,2,5,5- and 2,2,4,5-Tetramethylhexanes

The synthesis of 2,2,5,5- and 2,2,4,5-tetramethylhexanes was accomplished by the following reactions: (a) Oxidation of 2,4,4-trimethyl-1-pentene to 4,4-dimethyl-2-pentanone (methyleopentyl ketone), (b) oxidation of this ketone to *t*-butylacetic acid, (c) conversion of the acid to methyl-*t*-butylacetate, (d) reaction of the ester with *t*-butylmagnesium chloride to give 2,2,5,5-tetramethyl-3-hexanol, (e) dehydration of the carbinol to a mixture of 2,2,5,5-tetramethyl-3-hexene, 2,3,5,5-tetramethyl-2-hexene and 2,3,5,5-tetramethyl-1-hexene, and (f) hyrdogenation of

[6] The intermediate contained approximately 50 percent carbinol, and 50 percent ketone. The total quantity of carbinol oxidized in each batch was calculated to be 10.65 moles plus 1.2 moles of ketone in the intermediate.

the first-named alkene to 2,2,5,5-tetramethylhexane and of the last two alkenes to 2,2,4,5-tetramethylhexane.

(a) The oxidation of 2,4,4-trimethyl-1-pentene was carried out essentially in the manner disclosed by Whitmore, Homeyer, and Trent [37]. Several runs were made on olefin of 95 percent or higher purity. (The isolation of this olefin is described later.) In a typical run, 101 moles of alkene was oxidized during 10 days with sodium dichromate by the slow addition of sulfuric acid. There was obtained 1,800 g of acidic material and 9,360 ml of neutral oil, which, on distillation in column 3, gave 2,154 ml of forerun, 4,150 g (36.4 moles) 4,4-dimethyl-2-pentanone (bp 123° to 126° C) and 2,000 ml of residue. This yield of ketone is equivalent to 36 percent of the theoretical amount. The acidic material was found to be a complex mixture containing only minor quantities of trimethylacetic and *t*-butylacetic acid and was not further investigated.

(b) The hypohalite oxidation of the methylneopentyl ketone to *t*-butylacetic acid was accomplished by a modification of the reaction disclosed by Whitmore, Homeyer, and Trent [37]. These authors used sodium hypobromite (prepared from bromine and sodium hydroxide), whereas in the present work the less expensive, commercially available calcium hypochlorite was used. Several small preliminary runs were made to develop familiarity with the reaction before a large run was undertaken. Three large runs were made, one of which is described.

A solution of 14.0 kg of technical sodium hydroxide in 38 liters of water was prepared. This solution was cooled to 19° C and to it was added about 90 kg of cracked ice and 13 kg of commercial calcium hypochlorite (70% available chlorine). The temperature thereby obtained was about −4° C. The ketone (50 moles) was then added during 3 hr. The temperature of the reaction mixture remained below +5° C during this addition. An additional 25 kg of cracked ice was added and the mixture stirred for 10 hr, after which it was heated to 65° to 70° C for 5 hr. After cooling the mixture to 20° C, 19.7 liters of sulfuric acid was added slowly and the products steam distilled. The crude product was distilled in several batches from a 1-liter claisen flask. There was thereby obtained 4,070 g (31.3 moles, 63%) of acid collected between 180° and 190° C. No further purification of the acid was made.

(c) The methyl ester of *t*-butylacetic acid was made in the usual manner. In a typical run a solution of 4,140 g (35.7 moles) of acid and 300 ml of concentrated sulfuric acid in 10 liters (250 moles) of methanol was heated to reflux for two periods of 7 hr each. The crude product thereby obtained was distilled in column 5 and gave 3,560 g (27.4 moles, 76.7%) of ester, which was collected at 125° to 127° C.

(d) The preparation of 2,2,5,5-tetramethyl-3-hexanol was carried out by the use of the reaction described by Moersch [25], which is an adaptation of that used by Heyd [18].

To the Grignard reagent prepared from 326 gram atoms of magnesium and 326 moles of *t*-butyl chloride was added 6,815 g (52.4 moles) of methyl *t*-butylacetate during 8 hr. The reaction mixture was refluxed 7 hr each day for 3 days and allowed to stand each night. Decomposition was caused by dilute sulfuric acid (17 kg of concentrated acid and 20 kg of water and ice). The product was steam distilled, and the aqueous layer extracted with ether. The organic layers were combined and the ether removed in column 11. The residue was redistilled in columns 24 and 7, yielding 6,507 g of carbinol collected at 166° to 170° C. This is equivalent to 41.2 moles, or 79 percent yield. Moersch reported 85 percent yield [25].

(e) Three preliminary experiments were made on the dehydration of 2,2,5,5-tetramethyl-3-hexanol and on the rearrangement of the resulting olefins. In one run, 117 g (0.70 mole) of carbinol was passed over 256 g (330 ml) of alumina (Baker Hydralo, lot 91942) at 300° to 305° C at the rate of 47 g/hr. The catalyst tube was 2.5 cm in diameter. The water recovered amounted to 10.8 ml (0.6 mole, 86%). The product was dried and fractionated in column 17. The yield of decenes amounted to 70 percent (78% on basis of carbinol consumed), and consisted of 34.5 mole percent 2,2,5,5-tetramethyl-3-hexene, 35.2 percent 2,3,5,5-tetramethyl-1-hexene, and 30.2 percent 2,3,5,5-tetramethyl-2-hexene.

In another experiment, 118 g of carbinol was dehydrated under the same conditions, except that the rate was 98 g/hr. In this case, a yield of 46 percent olefins (73% on basis of carbinol consumed) was obtained. The mixture of olefins contained 34.8 percent 2,2,5,5-tetramethyl-3-hex-

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ene, 42.0 percent 2,3,5,5-tetramethyl-1-hexene, and 23.2 percent 2,3,5,5-tetramethyl-2-hexene.

To determine the extent of rearrangement of the olefins, a mixture of decenes was passed over the catalyst at 300° to 310° C at the rate of 44 g/hr. Analysis of the resultant mixture showed that the original mixture was isomerized as follows: 2,2,5,5-tetramethyl-3-hexene, from 13.5 to 16.8 percent; 2,3,5,5-tetramethyl-1-hexene, from 46.2 to 31.2 percent; and 2,3,5,5-tetramethyl-2-hexene, from 40.0 to 52.0 percent.

The bulk of the carbinol was dehydrated in the manner used in the first experiment. The resultant mixture was dried and distilled in column 5. The carbinol recovered was recycled for dehydration. In this way, 4,999 g of crude olefin mixture was obtained (86.6% yield). This mixture was separated roughly in column 5 into concentrates boiling at 121° to 127° C, 139° to 145° C, and 152° to 158° C, and intermediate fractions. A sample (500 ml) of each hydrocarbon was redistilled in column 17 for preparation of pure compounds. The impure fractions from each of these distillations were returned to the appropriate concentrate. These olefins have been identified previously [18, 25].

(f) Each of the olefin concentrates was hydrogenated separately, as was the combined intermediate. The latter two olefin concentrates gave the same paraffin and were combined for distillation. Purification of both paraffins was accomplished in column 18. The best 500-ml samples from each distillation were redistilled in column 17, and physical constants were measured on the best samples from these distillations.

24. 2,2,3,3-Tetramethylhexanes

This hydrocarbon was synthesized at Pennsylvania State College (Frank C. Whitmore) and purified at the Bureau. When received, the sample (2 gallons) contained chlorides, which were removed by boiling with alcoholic alkali. The product was washed, dried, and fractionated in columns 19 and 20. The best portion from one of these distillations was refractionated in column 17. Physical constants were determined on the best fractions from this distillation.

25. 3,3,4,4-Tetramethylhexane

The method of preparation of this decane is similar to that used in the preparation of 2,2,3,3-tetramethylpentane, and involved the reaction between ethylmagnesium chloride and 2-chloro-2,3,3-trimethylpentane.

In the exploratory synthesis, 2,3,3-trimethyl-1-pentene (boiling range 108.34° to 108.40° C, n_D^{20}=1.4170 to 1.4172) was converted to the chloride, 2-chloro-2,3,3-trimethylpentane, by reaction with dry hydrogen chloride at −30° C. The product was fractionated in column 4. The forerun of unchanged olefin was used in the preparation of more chloride. The chloride used in the coupling reaction was that collected between 81° and 82° C at 57 mm Hg.

To the Grignard solution prepared from 10 gram atoms of magnesium and 10 moles of ethyl bromide, there was added, during 7 days, 9.3 moles (1,382 g) of the chloride. On the twelfth day the mixture was worked up. The ether was removed from the organic layer and the residue refluxed 6 hr with alcoholic alkali (10% KOH) to remove chlorides. The washed, dried, chloride-free material was distilled in column 17.

A large run of the preparation of this hydrocarbon is in progress. From this run a considerably purer compound is expected.

26. 2,3-Dimethyl-1-butene and 2,3-Dimethyl-2-Butene

The preparation and properties of 2,3-dimethyl-2-butene, and 2,3-dimethyl-1-butene have been reported previously by this Bureau [7]. Although the 2,3-dimethyl-1-butene reported was relatively pure, the 2,3-dimethyl-2-butene was decidedly impure. The boiling range of the best sample of the latter was about 0.4° C, even after repeated fractionation, whereas other hydrocarbons prepared and reported in the same paper had boiling ranges of less than 0.01° C. The wide boiling range has been attributed to the presence of peroxides in the sample. This tendency to form peroxides is much more pronounced in the 2,3-dimethyl-2-butene than in the 1-isomer. As both alkenes result from the same reaction, the study of both compounds was repeated.

The method of preparing the alkenes was by dehydration of 2,3-dimethyl-2-butanol, by means of iodine. The carbinol was prepared by action of methylmagnesium bromide on methyl isobutyrate.

Several batches of methyl isobutyrate were made, in each of which 90 moles of methanol

and 30 moles of isobutyric acid were refluxed for 6 to 8 hr with 15 ml of concentrated sulfuric acid. The product was recovered by adding water, extracting the unchanged acid by sodium carbonate solution, and saturating the aqueous layer with salt to recover unused alcohol and dissolved ester. The combined, nonacidic organic layer was distilled in columns 3, 4, 5, and 6. Only constant-boiling (±0.1° C) material was reserved for subsequent steps. The yield amounted to 71 percent of the theoretical, based on original isobutyric acid.

In a typical run of the preparation of 2,3-dimethyl-2-butanol 42 moles of methyl isobutyrate was added to 90 moles of methylmagnesium bromide in 12 hr. After the reaction mixture had been allowed to stand for 15 hr, it was warmed for 4 hr and then treated with ice and dilute hydrochloric acid. The organic material was dried and distilled in column 6. After ether and unchanged ester had been removed, the carbinol was distilled at 76.4° to 76.6° C at 152 mm Hg. The yield was 3,120 g (73%, based on ester).

The dehydration of 2,3-dimethyl-2-butanol was accomplished by heating it with 1 gm of iodine per liter of carbinol. The olefinic material thereby obtained was roughly separated in column 4 and consisted of approximately 3 parts of 2,3-dimethyl-2-butene and 1 part of 2,3-dimethyl-1-butene. The residue from this distillation consisted of unchanged carbinol that had steam distilled during the dehydration step. This carbinol was returned to the dehydration process as it accumulated. In this way, a practically quantitative yield of alkenes was obtained.

Two charges of crude 2,3-dimethyl-2-butene were fractionated in column 1. The "middle cuts" from these distillations, the fractions of which had a constant refractive index (± 0.00005), were combined and amounted to 3.6 liters of material. The 2,3-dimethyl-1-butene was fractionated in like manner, and 3.5 liters of material was obtained. The two hydrocarbons were then subjected to distillation in column 5 under conditions designed to destroy any peroxides present and to prevent their formation in the distillate. This was accomplished by adding hydroquinone to the distillation charge and by keeping the column, take-off, and delivery systems flushed with nitrogen. In this way, thirty-three 100-ml fractions of each hydrocarbon were obtained.

For measuring the physical properties of these olefins the same apparatus and methods previously described were used, but care was exercised to displace air in the apparatus with nitrogen during the determinations. Refractive indices were measured in the usual manner. Peroxide numbers (moles of active oxygen in 1,000 liters of solution) were determined by the method of Yule and Wilson [43].

For 2,3-dimethyl-1-butene, fraction 17 was used for determination of refractive index and density. The peroxide number of this fraction was 0.03. Measurements of boiling points of this olefin were made with fractions 16 and 19. The distillate from these determinations contained an unmeasurably small amount of peroxide. The freezing point of 2,3-dimethyl-2-butene was made on fraction 17 (0.07 peroxide number). Refractive-index and density measurements were made on fraction 21 (0.03 peroxide number) and boiling-point measurements on fractions 18, 19, and 20 (0.04 to 0.06 peroxide number). The measured values of the properties are given in table 6.

Considerable difference of opinion exists regarding the freezing point of 2,3-dimethyl-1-butene. Schurman and Boord [30] report a "melting" point of −120° to −123° C on material having a boiling range of 0.4° C. Brooks, Howard, and Crafton [7] report a freezing point of −140.1° C on a sample of high purity, which, however, undoubtedly contained some peroxide. Kistiakowsky and coworkers [20], using a sample having a boiling range of 0.01° C for determining the heat of hydrogenation, reported that the material congealed to a glass at low temperatures. Two attempts were made in this work to freeze samples that were peroxide free, but both were unsuccessful. An attempt to freeze samples recovered from the boiling-point distillates, which had been exposed to air for 2 weeks, also failed. Attempts were made to freeze samples containing small amounts of 2,2,4-trimethylpentane; those samples containing 0.58 and 2.4 mole percent of this impurity failed to freeze. One sample containing 1.43 mole percent of 2,2,4-trimethylpentane gave an indefinite freezing point at −145.4° C. This value seems to substantiate the previous [7] value of −140.1° C, and would indicate a very low heat of fusion, which may be a controlling factor in the determination of the freezing point.

TABLE 6.—*Physical properties of compounds prepared*

nf = Material became very viscous or glassy without freezing to a crystalline solid.
nd = Material considered too impure to warrant determination of freezing point.
mp = Melting point.
LBI = Lower-boiling geometric isomer.
HBI = Higher-boiling geometric isomer.
CT = Mixture of geometric isomers.

Compound	Freezing point in air	Boiling point at 760 mm Hg	dt_B/dP at 760 mm Hg	ΔT 20 to 80 percent	Density at—		dD/dt 20° to 25° C	Refractive index at—		dn/dt 20° to 25° C	Date first preparation completed
					20° C	25° C		20° C	25° C		
	° C	° C	° C/mm Hg	° C	g/ml	g/ml	(g/ml)/° C	n_d	n_d	n_d/° C	
n-Pentane	−129.75	36.075	0.0388	0.006	0.62619	0.62133	−0.00097	1.35746	1.35480	−0.00053	January 1941.
2-Methylbutane	−159.9	27.853	.0386	.006	.61963	.61455	−.00102	1.35357	1.35057	−.00058	December 1939.
2, 2-Dimethylpropane	−16.60	9.508	[a].0361	.017							April 1942.
2-Methylpentane	−153.73	60.266	.0418	.002	.65285	.64848	−.00088	1.37141	1.36866	−.00055	January 1944.
3-Methylpentane	nf	63.265	.0426	.005	.66438	.65972	−.00093	1.37646	1.37376	−.00054	November 1940.
2, 2-Dimethylbutane	[b]−100.06	49.733	[b].0407	.004	.64923	.64422	−.00100	1.36873	1.36585	−.00058	May 1941.
2, 3-Dimethylpentane	nf	89.787	.0450	.002	.69510	.69060	−.00084	1.39193	1.38950	−.00049	August 1941.
2, 4-Dimethylpentane	−119.86	80.508	.0431	.003	.67315	.66879	−.00087	1.38165	1.37903	−.00053	May 1941.
2-Methyl-3-ethylpentane	−114.94 (mp)	115.653	.0477	.004	.71931	.71523	−.00082	1.40403	1.40173	−.00046	January 1941.
2, 2, 3-Trimethylpentane	[b]112.32	109.847	.0487	.002	.71608	.71201	−.00081	1.40280	1.40052	−.00046	August 1941.
2, 3, 3-Trimethylpentane	−101.6	114.767	.0491	.004	.72621	.72229	−.00079	1.40757	1.40521	−.00047	October 1940.
2, 2, 4-Trimethylhexane	−123.4 (mp)	126.54	.0503	.011	.71555	.71178	−.00076	1.40328	1.40095	−.00047	October 1942.
2, 2, 5-Trimethylhexane	−105.89 (mp)	124.092	.0485	.005	.70711	.70313	−0.0080	1.39956	1.39724	−.00047	July 1941.
2, 3, 5-Trimethylhexane	−127.9	131.37	.0492	.021	.72191	.71792	−.00080	1.40601	1.40365	−.00047	June 1941.
2, 2-Dimethyl-3-ethylpentane	−99.30	133.834	.0506	.002	.73478	.73100	−.00076	1.41227	1.41014	−.00043	September 1941.
2, 4-Dimethyl-3-ethylpentane	−122.4	136.717	.0504	.009	.73793	.73415	−.00076	1.41371	1.41146	−.00045	November 1941.
2, 2, 3, 3-Tetramethylpentane	−10.04	140.264	.0512	.009	.75676	.75300	−.00075	[d]1.42365	[d]1.42146	−.00044	December 1940.
2, 2, 3, 4-Tetramethylpentane	−122.2	133.010	.0501	.007	.73915	.73537	−.00076	1.41462	1.41242	−.00044	July 1941.
2, 3, 3, 4-Tetramethylpentane	−102.14	141.544	.0514	.002	.75489	.75112	−.00075	1.42222	1.42005	−.00043	November 1941.
2, 2, 3, 3-Tetramethylhexane	−54.03	160.310	.0538	.005	.76450	.76080	−.00074	1.42812	1.42606	−.00041	November 1943.
2, 2, 4, 5-Tetramethylhexane	nf	147.875	.0512	.011	.73542	.73165	−.00075	1.41321	1.41093	−.00046	October 1945.
2, 2, 5, 5-Tetramethylhexane	−12.64	137.457	.0500	.004	.71875	.71480	−.00079	1.40550	1.40315	−.00047	August 1945.
3, 3, 4, 4-Tetramethylhexane	nd	170.0	.046	.37	.7824	.7789	−.0007	1.4368	1.4346	−.0004	Do.
2, 4-Dimethyl-3-isopropylpentane.	−81.75	157.042	.0544	.012	.75826	.75460	−.00073	1.42465	1.42246	−.00044	March 1945.
2, 2, 3, 3, 4-Pentamethylpentane	−36.49	166.05	.0552	.039	.78009	.77675	−.00067	1.43606	1.43412	−.00039	February 1942.
2, 2, 3, 4, 4-Pentamethylpentane	−38.81	159.29	.0537	.052	.76702	.76362	−.00068	1.43069	1.42868	−.00040	October 1944.
3-Methyl-2-pentene (LBI)	−135.4	67.8	.039	.16	.6942	.6898	−.00088	1.4016	1.3989	−.00054	September 1942.
3-Methyl-2-pentene (HBI)	−138.5	70.5	.037	.17	.6986	.6942	−.00098	1.4045	1.4018	−.00054	Do.
2, 3-Dimethyl-1-butene	nf	55.641	.0429	.002	.67792	.67312	−.00096	1.39044	1.38745	−.00060	February 1944.
2, 3-Dimethyl-2-butene	−74.30	73.206	.0424	.006	.70795	.70336	−.00092	1.41221	1.40944	−.00055	October 1943.
2, 3, 3-Trimethyl-1-pentene	nf	108.4	.05	.27	.7352	.7308	−.00088	1.4174	1.4151	−.00047	April 1945.
2, 4, 4-Trimethyl-1-pentene	−93.56	101.437	.0459	.003	.71500	.71076	−.00085	1.40856	1.40601	−.00051	June 1943.
2, 3, 4-Trimethyl-2-pentene	−113.39	116.26	.0493	.082	.74342	.73914	−.00086	1.42736	1.42500	−.00047	July 1942.
2, 4, 4-Trimethyl-2-pentene	−106.51	104.914	.0470	.007	.72124	.71700	−.00085	1.41602	1.41350	−.00050	July 1943.
3, 4, 4-Trimethyl-2-pentene (CT)	nf	112.3	.05	.42	.7392	.7350	−.00083	1.4235	1.4210	−.00050	July 1942.
2, 3, 5-Trimethyl-2-hexene		73 (100 mm) 58 (50 mm)						1.4299			October 1940.
2, 3, 3, 4-Tetramethyl-1-pentene.		133.2	.051	.30	.7567	.7549	−.00076	1.4306	1.4283	−.00046	November 1941.
4-Methyl-3-isopropyl-2-pentene.	nf	138.0 96 (200 mm)	.046	.88	.7627	.7591	−.00072	1.4353	1.4328	−.00049	August 1940.
2, 4-Dimethyl-3-ethyl-2-pentene.	−93.5	129.97 88 (200 mm)	.0439	.073	.74392	.73997	−.00079	1.42346	1.42112	−.00047	Do.
4, 4-Dimethyl-3-ethyl-2-pentene (CT).	nf	134.03 94 (150 mm)	.0466	.060	.7561	.7521	−.00079	1.4309	1.4285	−.00049	August 1941.

[a] See reference [7].
[b] See reference [6].
[c] Calculated from data given in reference [2].
[d] The refractive indices of 2, 2, 3, 3-tetramethylpentane were determined by Leroy Tilton, of the Optical Instruments Section of this Bureau.

TABLE 6.—*Physical properties of compounds prepared*—Continued

Compound	Freezing point in air	Boiling point at 760 mm Hg	dB/dP at 760 mm Hg	ΔT 20 to 80 percent	Density at—		dD/dt 20° to 25° C	Refractive index at—		dn/dt 20° to 25° C	Date first preparation completed
					20° C	25° C		20° C	25° C		
	° C	° C	° C/mm Hg	° C	g/ml	g/ml	(g/ml)/° C	n_d	n_d	n_d/° C	
3, 3-Dimethyl-2-isopropyl-1-butene.	−78.2	122.21	0.0502	0.037	0.73614	0.73228	−0.00077	1.41669	1.41431	−0.00048	October 1941.
2, 3, 5, 5-Tetramethyl-1-hexene	nf	142.8	.049	.185	.7448	.7407	−.00082	1.4226	1.4203	−.00046	July 1945.
2, 3, 5, 5-Tetramethyl-2-hexene	nf	156.2	.049	.34	.7659	.7622	−.00074	1.4374	1.4351	−.00048	Do.
2, 2, 5, 5-Tetramethyl-3-hexene	−4.75	125.013	.0480	.010	.71673	.71223	−.0090	1.41148	1.40890	−.00052	Do.
2, 3, 3, 4, 4-Pentamethyl-1-pentene.	+38.66	158.75	.054	.039							September 1944.
2, 4-Dimethyl-3-isopropyl-2-pentene.	−55.3	152.4	.051	.34	.7680	.7637	−.00084	1.4377	1.4353	−.00047	February 1945.
3, 3-Dimethyl-2-t-butyl-1-butene.	−62.9	150.3	.052	.22	.7710	.7671	−.00077	1.4359	1.4339	−.00040	April 1944.
2, 3-Dimethyl-1, 3-butadiene		68.5-71.5			.7267			1.4388			May 1940.
3-Methyl-3-pentanol	−23.6	122.4	.039	.30	.8286	.8243	.00086	1.4186	1.4163	.00046	August 1941.
		80 (150 mm)									
2, 3-Dimethyl-2-butanol	−10.4	118.4	.037	.042	.8236	.8193	−.00086	1.4170	1.4148	−.00044	October 1943.
		76 (150 mm)									
3, 5, 5-Trimethyl-3-hexanol		71 (25 mm)			.8350			1.4352			July 1941.
2, 4-Dimethyl-3-ethyl-3-pentanol.	−16.0	177.9	0.48	.70	.8568	.8543	−.00089	1.4439	1.4416	−.00045	July 1940.
		96 (50 mm)									
2, 2-Dimethyl-3-ethyl-3-pentanol.	−19.0	174	.05	1.55	.8572	.8526	−.00091	1.4429	1.4405	−.00047	July 1941.
		94 (50 mm)									
2, 2, 3, 4-Tetramethyl-3-pentanol.	+12.8	173.4	.047	.83	.8565	.8523	−.00085	1.4405	1.4428	−.00047	Do.
		94 (50 mm)									
2, 4-Dimethyl-3-isopropyl-3-pentanol.	−14.7	194.5	.051	.77	.8632	.8591	−.00083	1.4480	1.4458	−.00043	December 1944.
		109 (50 mm)									
2, 2, 3, 4, 4-Pentamethyl-3-pentanol.	+42.1	194.4	.059	.38							February 1944.
2, 2, 4-Trimethyl-3-pentanone	−29.02	126.190	.0485	.007	.80654	.80229	−.00085	1.40596	1.40389	−.00042	June 1941.
2, 2, 4, 4-Tetramethyl-3-pentanone.	−25.24	153.521	.0521	.010	.82409	.82027	−.00076	1.41927	1.41712	−.00043	January 1944.
Ethyl Trimethylacetate	−89.55	118.35	.0458	.061	.85467	.84952	−.00103	1.39061	1.38821	−.00048	June 1941.
3-Chloro-2, 2, 3-Trimethylpentane.	−17.9	87 (62 mm)			.9066			1.4441			July 1942.
2-Chloro-2, 3, 3-Trimethylpentane.	+10.6	82 (57 mm)			.9105	.9065	−.00080	1.4457	1.4436	−.00042	June 1945.
2-Chloro-2, 3, 4-Trimethylpentane.		82 to 86 (60 mm)			.888			1.438			August 1942.
3-Chloro-2, 3, 4-Trimethylpentane.											
3-Chloro-2, 3-Dimethyl-2-butene.		32 (45 mm)									May 1940.

The presence of peroxides caused a marked change in the boiling ranges of these olefins. When samples of pure 2,3-dimethyl-1-butene were distilled in the boiling-point apparatus, the observed temperature changes (from 20 to 80% distilled) were less than 0.004° C. The same material, after exposure to air for 2 months showed a distillation range (20 to 80%) of 0.11° C. Still more pronounced is the effect of peroxides on 2,3-dimethyl-2-butene. Samples containing a small quantity of peroxide (peroxide number 0.04) distilled over a range of 0.007° C or less, but after this material had accumulated peroxides for 10 days, the distillation range was found to be 1.03° C.

In order to determine the rate of peroxide formation under normal laboratory conditions, samples of purified alkenes were allowed to stand at room temperature in contact with air. Periodically, portions were withdrawn and analyzed for peroxides. The results of these analyses are given in table 7.

TABLE 7.—*Rate of peroxide formation in 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene*

Time	Peroxide number (moles of active oxygen per 1,000 liters of solution)[a]	
	2,3-Dimethyl-1-butene	2,3-Dimethyl-2-butene
Hours		
0	0.10	0.30
2.5	.13	6.8
5.0	.18	11.6
10.0	.26	19.0
15	.35	24.8
20	.44	29.9
30	.65	39.7
40	.86	
50	1.09	

[a] For these hydrocarbons, at ordinary temperature, a peroxide number of 1 corresponds to approximately 0.012 mole percent peroxide impurity.

27. 3-Methyl-2-pentene (*cis* and *trans*)

The two geometric isomers of 3-methyl-2-pentene were prepared by dehydration of 3-methyl-3-pentanol, which was formed by action of ethylmagnesium chloride on 2-butanone.

To 53.8 moles of ethylmagnesium chloride was added 55.8 moles of 2-butanone in 5 liters of ether. The yield of carbinol (bp 75° to 80° C at 142 mm Hg) was 40 percent of the theoretical. The carbinol was dehydrated with β-naphthalene sulfonic acid to yield a mixture of olefins. A charge of 2,240 ml of the washed, dried olefin mixture was fractionated in column 2, which gave 240 ml of the lower-boiling (*cis*?) and 960 ml of the higher-boiling (*trans*?) isomers. Physical constants were measured on the best samples of each isomer. Analysis of the distillation curve showed that the original mixture contained 26 percent (by volume) of the lower-boiling and 74 percent of the higher-boiling forms.

The identification of these two olefins as *cis* and *trans* 3-methyl-2-pentene, rather than the isomers 3-methyl-2-pentene and 2-ethyl-1-butene, is based primarily on mass spectrometer studies. The two patterns formed by analysis of the compounds obtained are very nearly identical.[7] No third component was isolated from the distillation, although it is probable that one was present in small quantity.

28. Investigation of "Diisobutylene"

It was necessary to isolate large quantities of the two diisobutylenes, 2,4,4-trimethyl-1-pentene, and 2,4,4-trimethyl-2-pentene, in order to provide samples for engine studies and for the syntheses of 4,4-dimethyl-2-pentanone and trimethylacetic acid by oxidation. For this purpose, a considerable quantity (450 liters) of the commercial mixture was systematically fractionated.

The original material was separated into five "cuts", or concentrates, by fractionation in column 11. Because of limited pot capacity, it was necessary to perform this operation in batches. Corresponding cuts from each batch were combined. The data on these distillations are summarized in table 8.

Cut *A* (forerun) was an azeotrope containing a small quantity of 2,4,4-trimethyl-1-pentene with butyl alcohol and other polar compounds. This cut was not extensively investigated.

Cut *C* (58 liters), the intermediate between cuts *B* and *D*, was refractionated in column 11 to yield 34 liters of 2,4,4-trimethyl-1-pentene, which was combined with cut *B*; 14 liters of intermediate, which was not further investigated; and 9 liters of residue, which was added to cut *D*. The

[7] For this opinion and for the experimental work from which it is drawn thanks are due Leo A. Wall, of the mass spectrometer laboratory of this Bureau.

TABLE 8.—*Division of "diisobutylene" by preliminary fractionation*

Cut	Volume	Volume percentage of total	Boiling range [a]	Refractive index (n_D^{20})	Major constituents
	Liters	*Percent*	*° C*		
A	14	3.1	Below 101.5	1.392 to 1.4082	2,4,4-Trimethyl-1-pentene, butyl alcohol, other polar compounds.
B	264	57.8	101.5 to 102	1.4084 to 1.4088	2,4,4-Trimethyl-1-pentene.
C	58	12.6	102 to 104	1.4094 to 1.4127	Intermediate, mixture of 2,4,4-trimethyl-1-and 2-pentenes.
D	85	18.7	104 to 107	1.4150 to 1.4160	2,4,4-Trimethyl-2-pentene, and small quantities of 2,3,4-and 2,3,3-trimethyl-1-pentenes, and other octenes.
E	[b] 27	[b] 6.0	107 to 117	1.4207 to 1.4238	2,3,4-Trimethyl- and 3,4,4-trimethyl-2-pentenes.
Gas and loss		1.8			

[a] Cottrell boiling-point measurements on first and last fractions.
[b] Includes residue.

augmented cuts *B* and *D* were then designated as *B–1*, and *D–1*, respectively.

Cut *B*–1 (298 liters) was found to be about 96.7 percent pure 2,4,4-trimethyl-1-pentene; its freezing point was −96.5° C. A 170-liter portion from the middle of this cut was refractionated in three runs, and 72 liters of purified 2,4,4-trimethyl-1-pentene was obtained, comprising fractions whose freezing points were in the range −93.59° to −93.55° C. Physical constants were measured on one of the fractions of −93.55° C material. Those constants agree with those reported by Tongberg, Pickens, Fenske, and Whitmore [32]. This compound has been identified by ozonolysis by Whitmore and Church [34].

Cut *D*–1 (95 liters), a concentrate of 2,4,4-trimethyl-2-pentene, was refractionated (in 2 runs). From these distillations, there was obtained 49.3 liters of high-purity 2,4,4-trimethyl-2-pentene, composed of fractions whose freezing points were −106.62° to −106.58° C. A portion was refractionated in column 1 for isolation of a sample for physical-constants measurements. This compound was also characterized by Tongberg, et al. [32], and identified by Whitmore and Church [34].

The residue from distillation of cut *D*–1 was fractionated in column 1. From this distillation there was obtained two concentrates, designated *D*–2 and *D*–3.

Cut *D*–2 (745 ml, bp 106.8° C, n_D^{20}=1.4149 to 1.4152, d^{20}=0.7265) was probably an impure sample of 2,3,4-trimethyl-1-pentene. Kuykendall [21] obtained the following properties for this compound: bp 106.7° to 107.7° C, n_D^{20}=1.4146 ^{20}=0.726.

Cut *D*–3 (804 ml, bp 108.0° C, n_D^{20}=1.4162 to 1.4171, d^{20}=0.733) was a complex mixture in which 2,3,3-trimethyl-1-pentene was the probable major component. This partial identification is made by a comparison of the physical properties of cut *D*–3 with those of the 2,3,3-trimethyl-1-pentene isolated from Shell "hot-acid polymer." (See next section.) As only small quantities of these cuts (*D*–2 and *D*–3) were available, no extensive investigation was made on them.

Cut *E* was combined with the residue from the preliminary fractionations. The combined material (27 liters) was fractionated in column 11, and yielded 3.8 liters of 3,4,4-trimethyl-2-pentene (*cis* and *trans*, presumably) (bp 112.0° to 112.6° C, n_D^{20}=1.4235, d^{20}=0.739) and 4.5 liters of 2,3,4-trimethyl-2-pentene (bp 116.1° to 116.2° C, n_D^{20}=1.4275, d^{20}=0.7428). These two compounds were identified by comparison of their physical properties with those of pure 3,4,4-trimethyl-2-pentene and 2,3,4-trimethyl-2-pentene. The pure compounds were obtained by the distillation analysis of Shell "hot acid polymer", described in the next section, and by synthesis as described in section IV–20. Part of this sample of 3,4,4-trimethyl-2-pentene was oxidized to pinacolone. The entire sample of 2,3,4-trimethyl-2-pentene was hydrogenated to 2,3,4-trimethyl-pentane (bp 113.41° C, n_D^{20}=1.4038 to 1.4040).

An approximate analysis of the original diisobutylene (gas-free basis) was made by examination of the distillation curves. This mixture was found to contain.

	Percent (by volume)
2,4,4-Trimethyl-1-pentene	70. 0
2,4,4-Trimethyl-2-pentene	18. 7
3,4,4-Trimethyl-2-pentene	4. 6
2,3,4-Trimethyl-2-pentene	3. 7
2,3,4-Trimethyl-1-pentene, 2,3,3-Trimethyl-1-pentene, and other octene(s).	1. 0
Other compounds	2. 0

29. Investigation of "Hot Acid Polymer"

The investigation of "hot acid polymer" (Shell Oil Co.) was undertaken to isolate and purify some of the major constituents. The general method of operation was the same as that used in the investigation of "diisobutylenes," but for this work more efficient, higher-capacity stills (numbers 12, 13, 14, and 16) were available.

A total of 1,041 liters of crude polymer was subjected to preliminary fractionation in five batches. Corresponding cuts from the several batches were combined. In this way, the polymer was divided into five portions. The data on these fractionations are given in table 9.

Cut *A*, which contained butanol-2, was not further investigated. Likewise, the residue has not been studied.

TABLE 9.—*Division of "hot acid polymer" by preliminary fractionation*

Cut	Volume	Volume, percentage of total	Boiling range [a]	Refractive index n_D^{20}	Remarks
	Liters		°C		
A	38	3.7	<101	<1.408	Forerun.
B	260	24.9	101.0 to 109.7	1.408 to 1.420	2,4,4-Trimethyl-1 pentene. 2,3,4-Trimethyl-1-pentene. 2,3,3-Trimethyl-1-pentene.
C	246	23.6	110.1 to 112.0	1.421 to 1.423	3,4,4-Trimethyl-2-pentene.
D	169	16.2	113.0 to 116.0	1.425 to 1.426	2,3,4-Trimethyl-2-pentene.
E	208	20.0	>116		Residue.
Gas [b] and loss		11.6			

[a] Cottrell boiling-point measurements on first and last fractions.
[b] A preliminary distillation of 2 liters indicated over 10 percent of gas.

By refractionation of cut *B*, there was isolated the following materials:

Cut *B*–1: 103 liters, 2,4,4-trimethyl-1-pentene, bp 101.1° to 101.3° C/755 mm Hg, n_D^{20}=1.4084 to 1.4086.

Cut *B*–2: 9.5 liters, a mixture of close-boiling olefins, bp 107.0° to 107.1°C/756 mm Hg, n_D^{20}= 1.4144 to 1.4146.

Cut *B*–3: 8.0 liters, 2,3,3-trimethyl-1-pentene, bp 108.0° to 108.1°C/753 mm Hg, n_D^{20}=1.4173 to 1.4175.

A considerable amount of material between *B–1* and *B–2* has not yet been investigated. This intermediate contains 2,4,4-trimethyl-2-pentene, associated with at least two other compounds whose boiling points are near 105°C.

Cut *B–2* was refractionated. The presence of several compounds is indicated by the distillation data. A sample of *B–2* was hydrogenated. Analysis of the product showed the presence of about 30 percent of 2,2,3- and 70 percent of 2,3,4-trimethylpentanes.

Cut *B–3* was refractionated for isolation of a sample suitable for physical constant measurements. A sample of this material was oxidized to methyl *t*-amyl ketone (bp 130.8° to 131.2° C, n_D^{20}=1.4201), whose 2,4-dinitrophenylhydrozone melted at 111° to 112° C. Hydrogenation of a sample yielded 2,3,3-trimethylpentane (bp 114.5° C, n_D^{20}=1.4073).

Purification by refractionation of cut *C* gave 100 liters of purified 3,4,4-trimethyl-2-pentene, bp 111.7° to 111.9°/751 mm Hg, n_D^{20}=1.4231 to 1.4233. The best sample from this fraction was used to determine the physical constants. The presence of *cis* and *trans* isomers, which were only partially separated by the fractionation, causes the wide boiling range. It is thought that the sample reserved for physical-constant measurements contained more of the higher-boiling (*trans*?) isomer than of the lower-boiling compound. Oxidation of this compound by sodium dichromate produced pinacolone in 30 percent yield.

Redistillation of 120 liters of cut *D* gave 45 liters of 2,3,4-trimethyl-2-pentene, bp 116.0°C/754 mm, Hg, n_D^{20}=1.4271 to 1.4272.

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